INDUSTRIAL CHEMISTRY

AN ELEMENTARY TREATISE FOR THE
STUDENT AND GENERAL READER

BY

EMIL RAYMOND RIEGEL, PH.D.

PROFESSOR OF INDUSTRIAL CHEMISTRY
UNIVERSITY OF BUFFALO

WITH THE SUPPORT OF A LARGE
NUMBER OF COLLABORATORS

FIFTH EDITION

REINHOLD PUBLISHING CORPORATION
430 PARK AVENUE NEW YORK 22, N.Y.

ASIA PUBLISHING HOUSE BOMBAY

WILLIAM H. NICHOLS

Dr. William H. Nichols (1852-1930), a graduate of New York University (1870), founder of the Nichols Chemical Company in 1872 at Laurel Hill, Long Island, which company eventually established works at Capelton, Quebec, Troy and Syracuse, New York, and at Nichols, California. In March, 1899, Dr. Nichols formed the General Chemical Company by the consolidation of twelve separate chemical manufacturing companies. General Chemical Company was the first to develop the contact process for the manufacture of sulfuric acid in the United States, the introduction of which was an important milestone in the history of sulfuric acid making in this country.

In 1902, Dr. Nichols established the fund for the Nichols' Medal to be awarded for original work which could be expected to further stimulate research in chemistry.

During the First World War, Dr. Nichols was chairman of the Committee on Chemicals of the Advisory Commission of the Council of National Defense. He was president of the American Chemical Society 1918-19.

In 1920, Dr. Nichols was instrumental in forming the Allied Chemical & Dye Corporation, a consolidation of General Chemical Company, The Solvay Process Company, Semet-Solvay Company, The Barrett Company and National Aniline & Chemical Company, Inc. He was chairman of the board of Allied Chemical & Dye Corporation from its formation until his death in 1930.

660
R443 I

COPYRIGHT, 1949, BY
REINHOLD PUBLISHING CORPORATION

All rights reserved

ALLAMA IQBAL LIBRARY
49895

ST 01
RG1

J. & K. UNIVERSITY LIB.
Acc. No. 49895
Date 17.7.64

CATALOGED BY

FIFTH EDITION

Sixth Printing, 1960

Printed in the United States of America

THE GUINN CO., INC.
New York 14, N. Y.

Renan, addressing Pasteur, in a speech of welcome at the French Academy (1882):

"Permettez-moi de vous rappeler votre belle découverte de l'acide droit et de l'acide gauche. . . . Il y a des esprit qu'il est aussi impossible de ramener l'un à l'autre qu'il est impossible, selon la comparaison dont vous aimez à vour servir, de faire entrer deux gants l'un dans l'autre. Et pourtant les deux gants sont également nécessaires: tous deux se complètent. Nos deux mains ne se superposent pas; mais elles peuvent se joindre. Dans le vaste sein de la nature, les efforts les plus divers s'ajoutent, se combinent et aboutissent à une résultante de la plus majestueuse unité."

"Yo te bendigo, Vida
porque veo al final de mi rudo camino
que yo fuí el arquitecto de mi propio destino;
que si extraje las mieles o la hiel de las cosas,
fué porque en ellas puse hiel o mieles sabrosas:
cuando planté rosales, coseché siempre rosas."

AMADO NERVO
(Mexican poet)

Translation

"I bless thee, Life
For at the end of the long road I see
That I was the architect of my own destiny;
That if I extracted the sweet or the bitter
from things,
'Twas because I put into them the bitter
or the sweet:
When I planted rosebushes, it was roses
that I reaped."

Preface to the Fifth Edition

The second World War is gradually receding into history, leaving behind a world impoverished in many directions by destruction and by the interruption of the normal tenor of manufacturing and trade—yet a world which paradoxically is richer in certain areas. Such an area is the group of chemical industries. Prodigious efforts during the war years to produce substitutes for natural materials which blockade or conquest cut off from our shores, to manufacture novel products suddenly become indispensable in the war effort, to increase production in certain lines from a trickle to a stream, have resulted in advances in the chemical industries which must be given a place, a prominent place, in a work devoted to their study. And at the same time, if the book is to fulfill its mission, the older, still fundamental processes must be retained, perhaps in somewhat abbreviated form. As a result, it is but to be expected that the Fifth Edition of "Industrial Chemistry" will be slightly larger than the preceding one.

Again, the general scheme of the book has remained unchanged, but every page, every line for that matter, has been re-examined and either retained, deleted, or replaced, as its validity directed. Many chapters have almost no resemblance to their former selves, among others those on Glass, Water and Sewage, Utilization of Wood, Sugar, Petroleum, Photography. Large portions of other chapters have been replaced by the description of current processes.

In preparing the text for the Fifth Edition, it has been the privilege of the author to profit by the generous support of many collaborators, some of whom are fellow workers in earlier editions, others joining the group for the first time.

The new names in the list of distinguished specialists are the following: Alfred E. Badger, who joined with Donald E. Sharp in collaboration in the chapter on glass; George E. Symons, who collaborated on water and sewage; Eduard Farber, on the chemical utilization of wood; Charles Robert Downs, on tonnage oxygen; S. C. Collins on the reversing heat exchanger for oxygen; Edward F. Wesp, on rayon and cellophane; Lionel S. Birkett, of British Guiana, on sugar; William G. Ringle, on paints and varnishes; J. B. Sprowls, on pharmaceuticals and antibiotics; A. Robert Fowler, on two topics: chemical explosives, and chemical agents for war other than explosives; Edwin R. Theis, on leather; Raife G. Tarkington, on photography; W. J. Toussaint, on butadiene from alcohol; C. E. Morrell, on butadiene from refinery products; J. E. Mitchell, on styrene; James E. Latta, on synthetic liquid fuels; and Frank J. Soday, on the manufacture of GR-S.

Messrs. Horak, Sharp, Weston, Wilson, and Booth continued their valued collaboration of previous years.

A reference under the name of each collaborator and reviewer will be found in the index.

To the many collaborators who preferred to remain anonymous, my deep thanks are here expressed—a very inadequate reward. For them, as for the listed collaborators, the most satisfying reward is the knowledge that they have contributed to the education of our successors, the chemists and chemical engineers of tomorrow.

The author wishes furthermore to record his indebtedness to the officials in Government agencies, for uniformly courteous and prompt reply to requests, especially to E. W. Pehrson, Chief of the Economics and Statistics Division, Bureau of Mines; to Maxwell R. Conklin, Chief of the Industry Division, Bureau of the Census; to James H. Hibben, Chief of the Chemical Division, U. S. Tariff Commission; to P. Burke Jacobs, Assistant to the Director, Bureau of Agricultural and Industrial Chemistry, and to many others. He is similarly indebted to the editors of professional magazines for permission to reproduce illustrations, to the managers of several concerns for the photographs used, and for drawings prepared especially for the present volume; examples of the latter are Figures 189 to 193, 265, and 268.

The Fourth Edition has been translated into the Spanish and Italian languages. An authorized edition in English was printed and distributed in China under the auspices of the Department of State. The Fourth Edition had previously been reproduced by lithography in China, as the earlier editions had been, without authorization.

Comments and criticisms by readers will be gladly received.

EMIL RAYMOND RIEGEL

Buffalo, N. Y.
September 24, 1949.

TABLE OF CHEMICAL AND ALLIED MANUFACTURES

Table of Chemical and

For the year indicated on each line, with a few items from general manufactures taken from the United States Tariff Commission report "Synthetic Organic merce, Bureau of the Census, Industry Division, "Inorganic Chemicals and Survey of Manufactures" (s.m.); and from Minerals Yearbook, 1951, Depart-

Paper and paper board, 1953, s.m.	$3,623,123,000
Organic chemicals, n.e.c., 1953, s.m.	2,802,402,000
Bituminous coal and lignite, 1951, m.y.	2,626,030,137
Shoes, 1953, s.m.	1,861,835,000
Rubber tires and inner tubes, 1953, s.m.	1,821,338,000
Industrial inorganic chemicals, other than chlorine and alkalies, but including compressed and liquefied gases except L.P.G., 1953, i.c.	1,541,557,000
Pharmaceutical preparations, 1953, s.m.	1,514,234,000
Flat glass, glass containers, laminated glass, pressed and blown glass, and glassware, 1953, s.m.	1,501,754,000
Paints and varnishes, 1953, s.m.	1,455,080,000
Synthetic fibers, 1953, s.m.	1,196,071,000
Fertilizers, manufacturing and mixing, 1953, s.m.	918,573,000
Cleaning and polishing preparations, 1953, s.m.	912,459,000
Synthetic plastics and synthetic resins materials, but cellulose plastics not included, 1953, t.c.	837,536,000
Soybean oil mill products, 1953, s.m.	804,533,000
Toilet preparations, 1953, s.m.	679,630,000
Hydraulic cement (incl. portland cement), 1951, m.y.	623,003,439
Cottonseed oil mill products, 1953, s.m.	603,561,000
Synthetic (chemical) rubbers, 1953, s.m.	529,000,000
Copper, primary, smelter output from domestic ores, 1951, m.y.	450,495,000
Medicinal chemicals, 1953, t.c.	409,068,000
Inorganic color pigments, 1953, s.m.	362,033,000
Alkalies and chlorine, 1953, s.m.	357,476,000
Zinc, primary slab zinc produced in U.S., 1951, m.y.	321,619,718
Aluminum, primary production in U.S., 1951, m.y.	305,074,000
Gypsum products industry, 1951, m.y.	237,047,000

(Assembled on the occasion of a reprinting in 1955

Allied Manufactures

for comparison. Figures are money values, for shipments or sales, and are Chemicals 1953" (t.c.); from three publications from the Department of Com- Gases 1953" (i.c.), "1953 Annual Survey of Manufactures" and "1952 Annual ment of the Interior, Bureau of Mines, (m.y.).

Insecticides and fungicides, synthetic, 1952, s.m.	$208,578,000
Bricks and hollow tiles, 1953, s.m.	200,580,000
Explosives, 1952, s.m.	184,775,000
Clay refractories, 1953, s.m.	159,663,000
Halogenated hydrocarbons, 1953, t.c.	159,867,000
Sulfuric acid, total, 1953, i.c.	156,327,000
Lead, primary, refined, from domestic and foreign ores, 1951, m.y.	144,522,000
Linseed oil mill products, 1952, s.m.	139,364,000
Caustic soda, total, 1953, i.c.	135,409,000
Sodium carbonates, 1953, i.c.	119,176,000
Synthetic ammonia, 1953, i.c.	100,224,000
Phosphorus, elemental, white (yellow) and red, 1953, i.c.	71,962,000
Sewer pipe, vitrified, 1953, s.m.	61,117,000
Crude artificial abrasives produced in the United States and Canada, 1951, m.y.	51,102,000
Flavors and perfume materials, 1953, t.c.	46,528,000
Ammonium nitrate, fertilizer grade, 100% NH_4NO_3, 1953, i.c.	45,446,000
Sulfated and sulfonated acyclic surface-active agents, 1953, t.c.	33,923,000
Methanol, synthetic, 1953, t.c.	27,943,000
Carbon disulfide, 1953, t.c.	23,536,000
Formaldehyde, 37% by weight CHOH, 1953, t.c.	20,623,000
Butyl alcohols, 1953, t.c.	14,358,000
Silver nitrate ("sold on open market" only), 1953, i.c.	12,875,000
Synthetic nitric acid, 1953, i.c.	12,173,000
Acetic acid, synthetic, 100%, 1953, t.c.	11,699,000
Salt cake, crude, technical, 1953, i.c.	11,215,000
Calcium chloride, solid and flakes, 1953, i.c.	9,815,000
Ethyl acetate, 85%, 1953, t.c.	7,126,000
Naphthenic acid salts (paint driers), other than copper naphthenate, 1953, t.c.	6,919,000
Iodine, resublimed, 100% I_2, 1953, i.c.	246,000

of the Fifth Edition of the Industrial Chemistry).

WHAT "THINGS CHEMICAL" ARE WORTH.

(Chiefly value as first produced at mine or works.)

Bituminous coal, average value, f.o.b. mines 1948, short ton	$ 4.95
Iron ore, 51% Fe, May 1948, long ton	6.20
Iron ore, crude ore, all kinds, average for 1946, at mine	3.07
Salt, NaCl, short ton, average for 1946, at mine, all forms	2.97
Rock salt, carlots, in bags, delivered in New York City, 1946, short ton	14.20
Sulfuric acid, 60° Bé, tank car lot, f.o.b. works, April 1949	13.75
Soda ash, average for 1947, at works	18.50
Sulfur, crude, bulk, at mines, 1949, short ton	18.00
Lime, chemical and industrial, short ton, 1946	8.52
Pig iron, no. 2 foundry, Philadelphia, July 1949, short ton	50.56
Caustic soda, liquid, on basis of 100% NaOH, short ton 1947.....	38.60
" " flakes " " " " " " "	61.90
Chlorine, liquid, 1947, short ton	42.50
Ammonia anhydrous, value at works, short ton, 1947	63.00

Table of Contents

PAGE

PREFACE TO THE FIFTH EDITION v

TABLE OF CHEMICAL AND ALLIED MANUFACTURERS viii

WHAT "THINGS CHEMICAL" ARE WORTH, TABLE x

CHAPTER

1 SULFURIC ACID:
PART I. THE CHAMBER PROCESS 1
Including the ammonia oxidation unit as source of nitre gas.

PART II. THE CONTACT PROCESS 20
Including vanadium pentoxide masses and platinum masses.

2 NITRIC ACID FROM SODIUM NITRATE, CHILE SALTPETER, MIXED ACID, IODINE, HYDROFLUORIC ACID, ALUMINUM SULFATE 43

3 SALT, SODA ASH, SALT CAKE, HYDROCHLORIC ACID, GLAUBER SALT, SODIUM SILICATE, BROMINE 56
Including calcium chloride from brines.

4 SODIUM SULFIDE, SODIUM THIOSULFATE (HYPO), ANHYDROUS BISULFITE OF SODIUM, SODIUM HYPOSULFITE 79

5 CAUSTIC SODA AND CHLORINE 89
Including high test hypochlorite, and liquid chlorine.

6 SYNTHETIC NITROGEN PRODUCTS—THE FIXATION OF ATMOSPHERIC NITROGEN—DIRECT AMMONIA, CYANAMIDE, NITRIC ACID FROM AMMONIA BY CONTACT CATALYSIS 111

7 PHOSPHATES, PHOSPHORIC ACID, BAKING POWDERS 134
Including superphosphate, triple superphosphate, trisodium phosphate, monocalcium phosphate.

8 FERTILIZERS, MIXED FERTILIZERS, POTASSIUM SALTS, NATURAL ORGANIC FERTILIZERS, SYNTHETIC UREA 147
Including ammoniated superphosphates, sodium nitrate pellets.

9 PORTLAND CEMENT, LIME, AND GYPSUM PLASTER 163
Including H. E. S. cement.

10 CERAMIC INDUSTRIES 177
Including pottery, building bricks, firebricks, vitrified enamel.

11 STRUCTURAL GLASS, GLASS CONTAINERS, OPTICAL GLASS, SPECIAL GLASS 194
Including window glass, plate glass, safety glass, glass construction blocks, bottle-blowing machines, fibrous glass, photosensitive glass.

12 FUELS, STEAM BOILERS, HYDROELECTRIC POWER, STEAM POWER, AND PRODUCTION OF COLD 224
Including water-cooled furnace, diphenyl and mercury vapor boilers, solid carbon dioxide or "Dry Ice," household refrigeration.

13 WATER FOR MUNICIPAL AND INDUSTRIAL USE; SEWAGE AND INDUSTRIAL WASTE DISPOSAL 251
Including softening and deionization of water.

14 THE DISTILLATION OF COAL FOR GAS, COKE, TAR AND AMMONIA 277
Including the Hot Actification sulfur recovery process.

CHAPTER PAGE

15 COMBUSTIBLE AND ILLUMINATING GAS, WATER GAS, PRODUCER GAS AND NATURAL GAS 298
Including underground storage of natural gas.

16 THE CHEMICAL UTILIZATION OF WOOD: EXTRACTION, HYDROLYSIS, DISTILLATION 309
Including sugar from wood, the Oregon plant, direct acetic acid, acetic anhydride, turpentine and rosin.

17 PRODUCTS OF THE ELECTROTHERMAL FURNACE 329
Including artificial graphite electrodes, silicon carbide, fused aluminum oxide grinding wheels, electro-orientation, calcium carbide.

18 PRODUCTS OF THE ELECTROLYTIC FURNACE (ALUMINUM, MAGNESIUM, SODIUM) AND PRODUCTS OF THE ELECTROLYTIC CELL OTHER THAN CAUSTIC 346
Including ammonium persulfate, ninety per cent hydrogen peroxide, sodium peroxide, sodamide, sodium cyanide.

19 INDUSTRIAL GASES 369
Including hydrogen, helium, oxygen, tonnage oxygen, nitrogen, liquid nitrogen, argon, neon and neon signs, fluorescent Mazdas, sulfur dioxide, nitrous oxide, acetylene.

20 PROCESSES BASED ON THE ACTIVITY OF YEASTS AND BACTERIA 393
Including ethyl alcohol from corn, industrial alcohol, brewing industry, absolute alcohol. acetone, lactic acid, citric acid, and vinegar.

21 CELLULOSE FROM WOOD: PULP AND PAPER 416

22 SYNTHETIC TEXTILE FIBER 443
Including rayon, staple rayon, nylon, cellophane, bottle seals, cellulose sponge.

23 CANE SUGAR, BEET SUGAR, CORN STARCH AND GLUCOSE 468
Including direct consumption sugars, Plantation White, Celotex, glutamic acid, corn sugar.

24 PETROLEUM AND ITS PRODUCTS; SYNTHETIC LIQUID FUELS; PETROCHEMICALS . . 487
Including the seismic method. and the "halo" method for discovery, reserves, classification of crudes, straight, natural and cracked gasoline, Thermofor Catalytic, Fluid Catalyst, Houdryflow Cracking processes, thermal cracking, solvent purification of lube fractions, antiknock compounds, octane number, Hydroforming, Alkylation, one hundred octane aviation gasoline. iso-octane. ozokerite.

25 SYNTHETIC AND SEMI-SYNTHETIC ORGANIC CHEMICALS 533
Including derivatives of acetylene, acetic acid, chlorinated hydrocarbons, the Reppe chemistry; derivatives of ethylene, ethylene oxide, glycols; Oxo process, nitroparaffins; catalytic hydrogenation and controlled oxidation of hydrocarbons, phthalic anhydride, maleic anhydride: manufacture of catalysts and their uses, table.

26 DYE APPLICATION 565
Including Developed Dyes, ice colors, Naphthol AS, Fast Color Salts, Rapidogens, direct dyeing.

27 THE MANUFACTURE OF DYE INTERMEDIATES 580

28 THE MANUFACTURE OF DYES 597
Including a classification, Indigosols, Phthalocyanines.

29 ANIMAL AND VEGETABLE OILS, FATS, AND WAXES 628
Including the Anderson expeller, Soybean oil, catalytic hydrogenation of oils.

30 ESSENTIAL OILS, PERFUME SUNDRIES, FLAVORS; PHARMACEUTICALS, ANTIBIOTICS 645
Including penicillin and streptomycin.

31 PIGMENTS, PAINTS, VARNISHES, LACQUERS, PRINTING INKS 666
Including "high" and "low" viscosity "cotton," lacquer enamel, ripple enamel, carbon black.

32 SOAP, FATTY ACIDS, GLYCERIN, SYNTHETIC DETERGENTS 686
Including synthetic glycerin.

33 CHEMICAL EXPLOSIVES 705
Including R D X, Haleite, P E T N.

CHAPTER PAGE

34 CHEMICAL FACTORS OTHER THAN EXPLOSIVES IN WARFARE 723
Including incendiaries, Napalm, Pyrogel (goop), screening smokes, Doron.

35 SYNTHETIC RESINS, SYNTHETIC PLASTICS 734
Including injection molding, transfer molding, formaldehyde, synthetic phenol.

36 LEATHER, GELATIN, AND GLUE 759
Including pellet glue, and a method for drying glue.

37 PHOTOGRAPHIC FILMS, PLATES, AND PAPERS; COLOR PHOTOGRAPHY, LITHOGRAPHY 773
Including Kodachrome, Ektachrome, Ansco Printon.

38 INSECTICIDES AND FUNGICIDES 786
Including synthetic organic insecticides, aerosols, sulfur.

39 RUBBER 802
Including synthetic rubbers, the manufacture of butadiene and styrene, extractive distillation, latex foam.

40 PATENTS 833

41 APPLIANCES USED BY THE CHEMICAL ENGINEER—I. PUMPS, FANS, BLOWERS AND COMPRESSORS 844

42 APPLIANCES USED BY THE CHEMICAL ENGINEER—II. FILTERS 853

43 APPLIANCES USED BY THE CHEMICAL ENGINEER—III. EVAPORATORS, DRIERS, COTTRELL PRECIPITATOR, AND OTHERS 866

44 APPLIANCES USED BY THE CHEMICAL ENGINEER—IV. CRUSHERS, DISINTEGRATORS, PULVERIZERS 879
Including bucket elevator, screens.

45 MATERIALS OF CONSTRUCTION USED BY THE CHEMICAL ENGINEER 891
Including the making of iron castings.

46 INSTRUMENTS OF CONTROL USED BY THE CHEMICAL ENGINEER 904
Including hydrometers, psychrometers, air conditioning, Pitot tube, Venturi tube, Ranarex analyzer, Carbometer, unit operation.

47 PIG IRON 924
Including wrought iron.

48 STEEL 936
Including rimming heat, killed heat, continuous strip mill, columbium in stainless steels, nitriding for case hardening.

49 COPPER, LEAD, ZINC, TIN, MERCURY 957
Including columbium, nickel, and indium.

50 GOLD, SILVER, PLATINUM, RADIUM, URANIUM, THORIUM, AND CERIUM 975
Including the atomic reactor, neptunium, plutonium, tungsten, vanadium.

APPENDIX 993

INDEX 1001

(NOTE: In the text, the number preceding the running head for the right-hand pages indicates the chapter number.)

In the house of chemistry, sulfuric acid is the man-of-all-work. Ever ready to labor, with a multiplicity of talents, he has been sought in years past, and still is today. Threats to displace him in at least some of his functions have been frequent, but he counters by uncovering new and unexpected services; so he is still with us, as prized as ever, and even more powerful. During the Civil War, an entire year's production for the whole country was only 40,000 tons; that quantity is now the production for one and one-half days.

Chapter 1

Sulfuric Acid—Part I: The Chamber Process

Sulfuric acid is manufactured either by the chamber process or by the contact process. In the chamber process the acid produced is rather weak, about 70 per cent H_2SO_4; the contact process produces 100 per cent acid and stronger grades containing the anhydride SO_3 in excess (the oleums). The chamber process is the older; it is characterized by comparatively large reaction chambers made of sheet lead, and by the use of a gaseous working agent (catalyst). In its original form, it represented the leisurely gait of the nineteenth century; it has maintained its place mainly because its product is concentrated enough and pure enough for the manufacture of superphosphate of calcium, a fertilizer. The contact process, on the other hand, produces the strong acid necessary for certain chemical reactions, such as those involved in the manufacture of dye intermediates. This process is characterized by the use of a solid "contact" substance, such as finely divided platinum, vanadium pentoxide, or ferric oxide.

The number of chamber acid plants reporting production decreased to a low in 1935, then increased in 1937, decreased slightly in 1939, and now shows a gain of 6 in 1945 over the 1939 figure.

U. S.	1929	1935	1937	1939	1945
Chamber sets	141	71	98	95	101
Contact plants	42	63	70	70	88

In production, the chamber acid plants lag behind the contact plants:

	1945
Chamber acid (as 100% H_2SO_4)	3,169,197 short tons (33.3% of total)
Contact acid (as 100% H_2SO_4)	6,352,939 short tons (66.7% of total)

The contact acid has gained in its percentage of the total production at a steady rate; in 1921, its percentage was 25.2% of the total; in 1923, 27.6%; in 1925, 29.2%; in 1929, 36.2%; in 1935, 47.2%; in 1937, 48.9%; in 1939, it passed 50%, reaching 55.5%; in 1942, it was 62.4%; in 1944, 64.8%; in 1945, as the table shows, 66.7%. The trend is due to the development of extremely compact installations for manufacturing sulfuric acid with vanadium masses, and to the standardization of such plants. This development in turn has been favored by the availability of brimstone at reasonable prices. Another reason for the greater growth of the contact process is that by it, acid of any strength, including the oleums, may be pre-

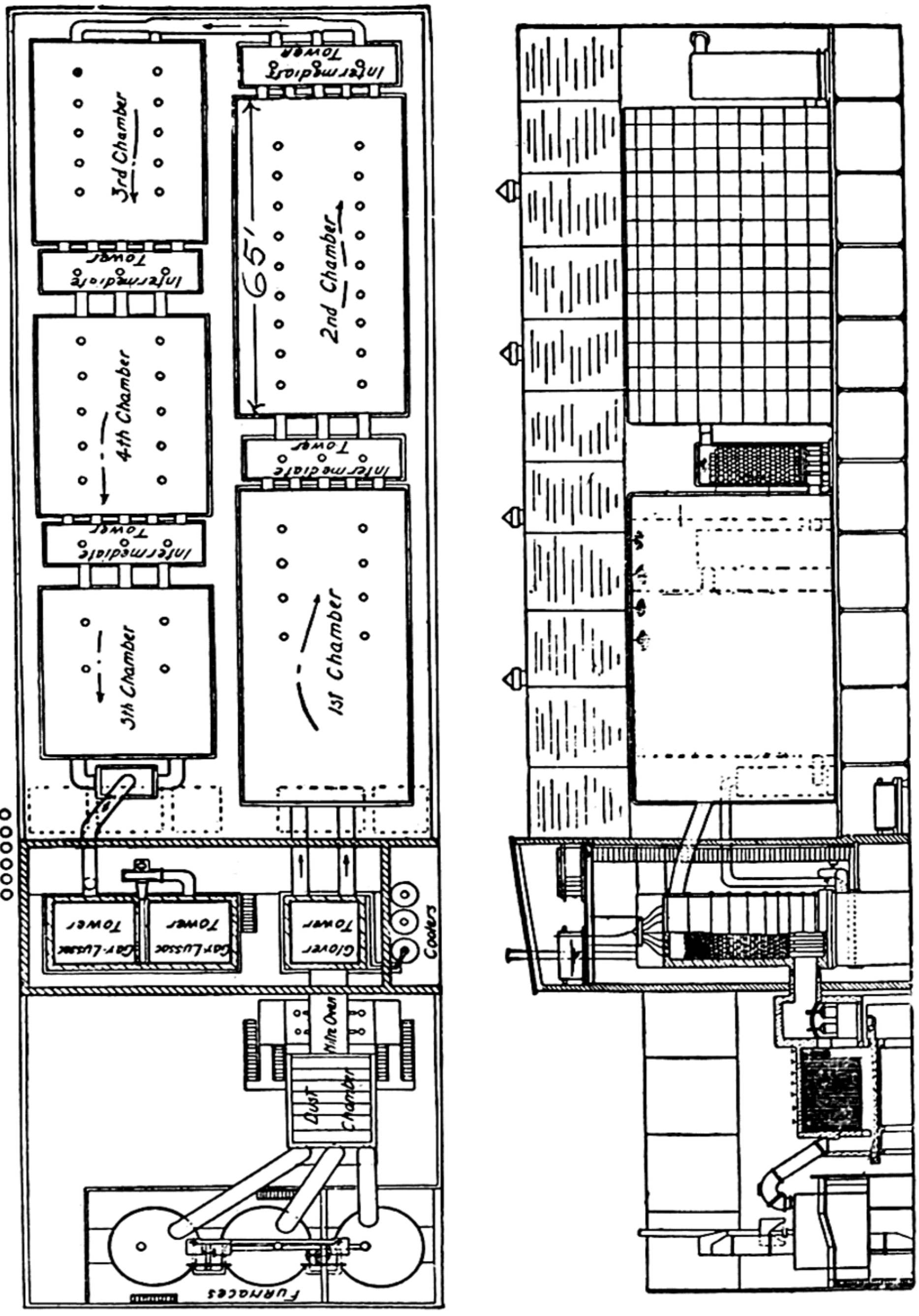


FIGURE 1.—A complete sulfuric acid chamber plant, with 3 furnaces, dust chamber, nitre pot, Glover tower, five rectangular chambers, the special intermediate towers (5), Gay-Lussac towers, acid lifts, acid coolers. One-third of the acid produced in this set (90 tons per day) is made in the intermediate towers; the first four are 25 feet high, 6 feet wide, 28 feet long. (Courtesy of the Chemical Construction Corpn., New York.)

pared with no other difficulty than diluting for the lower strengths; whereas by the chamber process, acid stronger than 55° Bé. can be made only by an additional operation, and oleums cannot be prepared at all. Nevertheless, the outlook for the chamber process is by no means dark, particularly in its more recent, water-cooled form, as will be seen later.

In the operation of the chambers, the potting of nitre is now almost obsolete. The "burning" of the cheaper ammonia to produce the necessary oxides of nitrogen permits a more intensive reaction; a slightly greater loss of nitric oxide can be tolerated. One pound of ammonia [NH_3] produces as much nitric oxide as five pounds of 100 per cent sodium nitrate.

A plant does not necessarily confine itself to one process,[1] but may operate both, diluting the stronger contact acid with the weaker chamber acid to produce medium strengths. In 1945, there were 15 plants operating both processes.

The principal commercial strengths of chamber acid are:

50° Bé. acid (chamber acid)	62.18%	H_2SO_4[2]
55° Bé. acid (chamber acid)	69.65	"
60° Bé. acid (chamber acid, concentrated by heat)	77.67	"
66° Bé. acid (oil of vitriol, concentrated by heat)	93.19	"

A table for converting Baumé degrees to specific gravities will be found in the Appendix.

The strength of the acid is judged by a hydrometer test, with the hydrometer graduations in Baumé degrees (*see* Chapter 46). For the strengths up to 66° Bé. (93.19 per cent H_2SO_4), that is satisfactory; between 93.19 and just above 100 per cent H_2SO_4, the electrical conductivity is a reliable and convenient method. Between 8 and 56 per cent free SO_3, the oleums may be tested with a hydrometer; below and above these figures, by titration. The commercial strengths of oleums are 15, 20, 26, 30, 45, 60, and 65 per cent free SO_3.

In order to manufacture sulfuric acid by the chamber process, there are needed: (a) burners for lump ore, rotary shelf burners for fines, or burners for brimstone sulfur; (b) a Glover tower; (c) a set of chambers preceded by the nitre pot or an ammonia burner; (d) a Gay-Lussac tower, which may be one tall structure or several shorter ones, interconnected; (e) storage tanks, distributing tanks, and pumps.

A specific set with a daily capacity of 25 tons of 55° Bé. acid per day is shown to scale in Figure 2, and will be described. It represents the older practice, even to the nitre pot. With this plant as a background, the important more recent developments will readily be placed and appreciated.

[1] A map and list showing the distribution of sulfuric acid plants, by types, in the United States, for 1945, will be found in "Facts for Industry," Series M19A.1-05, Bureau of the Census, released June 5, 1946. The map shows the division of the country into 15 regions for this purpose. The highest production is that of the Baltimore region, with 876,708 tons of new acid; the second highest is the New York region, with 843,285 tons. Next are three regions which have about the same production, just over 731,000 tons; they are, in order, Great Lakes, Gulf Coast, and Chicago. The various regions differ enormously in size.

[2] Taken from the table published by the Manufacturing Chemists' Association of the United States. The relation of Baumé degrees and decimal specific gravity is as follows: Baumé degrees = 145 − (145 ÷ specific gravity).

(a) **Lump Burners.** The source of sulfur dioxide in this 25-ton set is iron pyrite, FeS_2, a very heavy, yellow ore, also called fool's gold. In size it is two-thirds nut, one-third pea. There are 30 burners, mere fire-places, each 5 feet broad, 6 feet deep and 6 feet high, with cast-iron grate bars and brick walls. Each receives a single charge of 1000 pounds per day. In order to start the ore, coke must be used, but once started, the ore supports its own combustion. Air is admitted under the grate bars, through a number of

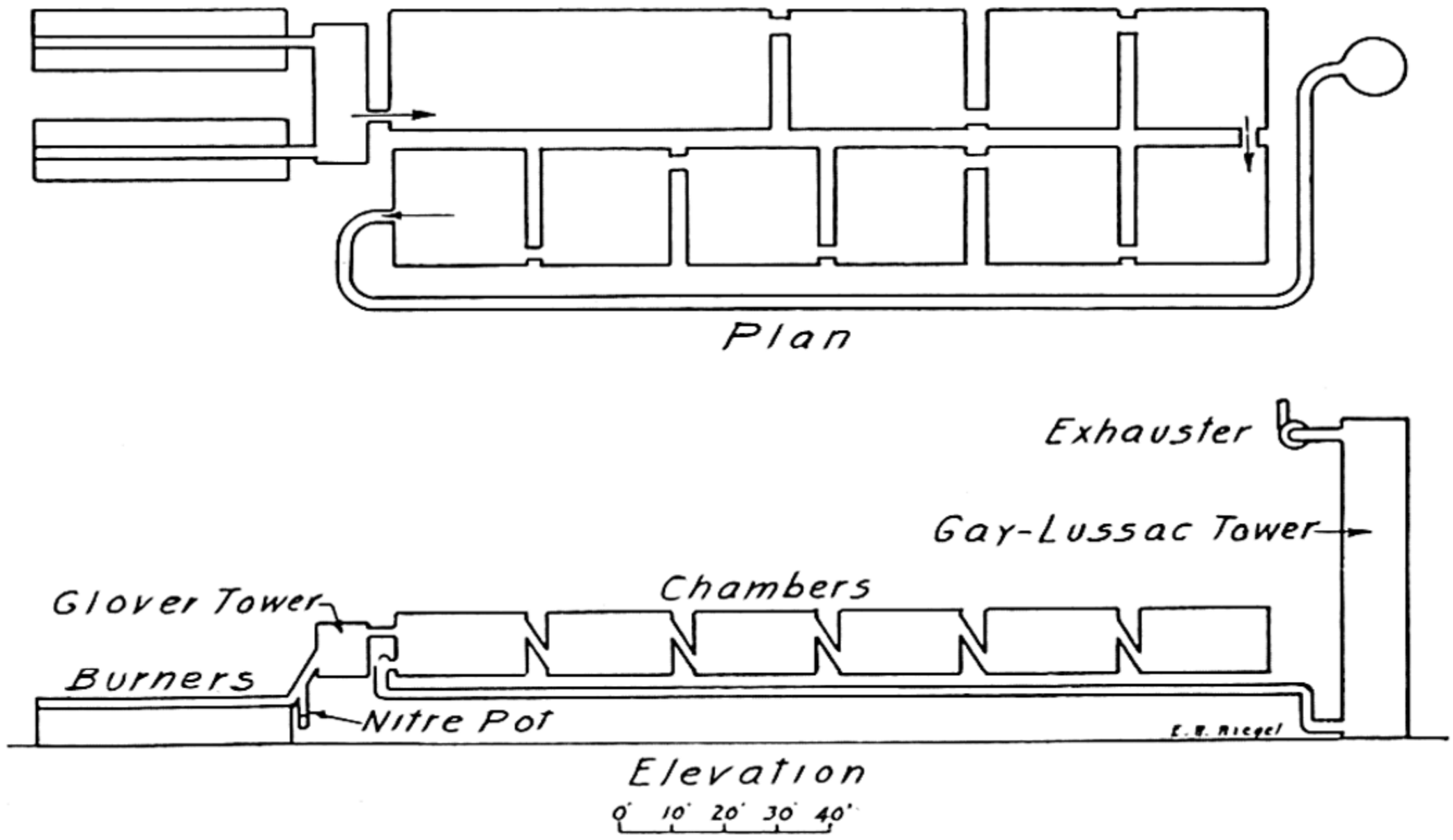


FIGURE 2.—A plant for the manufacture of sulfuric acid by the chamber process, with burners for lump ore.

2-inch holes which may be closed at will; the amount of air, and therefore the percentage of sulfur dioxide in the "burner gas," is regulated here. The burner gas with all its heat passes through a flue to the nitre pot, and thence into the base of the Glover tower. The iron is left on the grate in the form of the dark red oxide, Fe_2O_3, which is discharged by shaking the grate. The reaction is $4FeS_2 + 11O \rightarrow Fe_2O_3 + 8SO_2$.

(b) Glover Tower. The Glover tower is a rather low rectangular box made of sheet lead supported by an outer steel frame and filled with quartz of assorted sizes or with Rashig rings. The acid collected at the base of the Gay-Lussac tower, rich in dissolved nitrous fumes, $NO + NO_2$, is elevated to the top of the Glover tower, and passes down the latter, together with water, which dilutes it and releases the dissolved nitrogen oxides. Up the tower passes the hot burner gas, carrying away the nitrogen oxides, and the water as steam. The Glover acid, on issuing from the bottom of the tower, passes through lead receiving tanks, where it is cooled by water from 130° F. (54° C.) to 60-70° F. (15-21° C.). There are, for example, three circular tanks, jacketed for water, and filled with upright lead coils through which water circulates. The acid from one tank must pass down and under an internal curtain before rising and overflowing to the next. The water

is cooled in a spray tower and is used over again. A portion of the cold acid is elevated by means of a pump to a small tank over the Gay-Lussac tower, from which it is fed gradually through a lead distributor and an elaborate system of small lead pipes, each with a U-bend forming a seal, to every part of the packing in the tower. The balance of the cold acid is "made acid" and goes to storage.

(c) Chambers. The set has a large first chamber, with a floor 75 by 26 feet; a second chamber, 35 by 26 feet; and eight smaller chambers 26 by 28 feet. The height for all is 14 feet. The walls, roof, and floor are of sheet lead, with the seams "burned" with lead, that is, melted with an air-hydrogen blowpipe; the lead is supported on an outer frame of wood or steel. The chambers have a bell construction, that is, the side walls hang free, and merely dip in the acid carried by the bottom tray. The acid forming the seal is in sight, and its height may be measured or observed.

(d) Gay-Lussac Tower. The Gay-Lussac tower is used to recover as far as possible the nitrogen trioxide gas which leaves the last chamber with the nitrogen and excess oxygen, and would otherwise be lost to the system. The tower is 70 feet high, circular, and has a diameter of 13 feet. It is made of lead supported by an outer steel frame and is filled with quartz lumps, graduated in size, the largest being on the bottom. The cold Glover acid passes down the tower; up the tower pass the gases from the tenth chamber; the descending acid dissolves the nitrogen oxides, and allows the other gases to escape. The absorption is never perfect. Nitrogen oxides, in the proportion of $NO+NO_2$, form a yellow gas which is soluble in 60° Bé. sulfuric acid; the strength of the solution after passage through the tower fluctuates between 1 and 2 per cent apparent N_2O_3; this is now the "Gay-Lussac acid," also called "nitrous vitriol"; when water is added to such a solution, the gas is liberated and passes out.

The marketable chamber acid is allowed to accumulate in the chambers, so that its level gradually rises. When the amount collected is sufficient, it is syphoned or pumped to a storage tank, or to a railroad tank car, ready for shipment. It is customary to use the chambers for storing the acid as it is made.

Since 1918, acid-proof masonry has been successfully applied to the construction of Glover and Gay-Lussac towers.[3]

(e) Auxiliary Devices. These are a nitre pot, set in an enlargement of the flue leading the burner gases to the Glover box; acid eggs, or blowcases, into which acid is run by gravity, and forced up a long pipe to the desired point by compressed air; and distributors, to divide the acid from a central pan at the top of a tower into a number of small streams so that all parts of the packing may be wetted. The nitre pot has been largely replaced by an ammonia burner, and the blowcases are giving way rapidly to the small centrifugal pumps of special metal. In addition, a Venturi pipe to measure the flow of gas, a fan to pull the gases through the chambers and towers, and lead syphons and lines to transfer the finished acid to storage tanks are necessary.

[3] "Recent developments in the manufacture of sulfuric acid," S. F. Spangler, *Ind. Eng. Chem.*, 21, 417 (1929).

In brief, then, the manufacture of the acid is as follows: Pyrite or sulfur is burned to produce sulfur dioxide; this oxide combines with oxygen and water, by the agency of nitric oxide, to form sulfuric acid. The Gay-Lussac tower is not needed for the reaction itself; it is a device for conserving the nitrogen oxides. Control of the reaction, so that the loss of the costly nitre gas will be a minimum, is the main problem.

In the cast-iron nitre pot, the nitre is covered with Glover acid; the heat of the burner gas causes the gradual evolution of nitric acid, which passes into the burner gas and there is reduced by sulfur dioxide to nitric oxide and nitrogen dioxide. These nitric oxides, with more or less moisture, are commonly spoken of as "nitre gas." The ammonia burner may be placed where the nitre pot was, and its gas delivered to the sulfur gas entering the Glover tower; a not infrequently selected place of entry, however, is after the Glover, just at the entrance to the first chamber.

The observations made by the "chamber man" in order to follow the reaction are: analysis of burner gas; temperature in the first and last chambers; sulfur dioxide analysis in the last chamber; color of the gas, and fog, at the exit of the last chamber, observed by means of a glass globe set in the line; depth of the yellow color of the gas at the exit from the Gay-Lussac tower; specific gravity of the drips from a lead table placed inside each chamber and from two tables in the first chamber; titration of Gay-Lussac tower acid for nitrogen trioxide; gauge reading at the Venturi meter, and readings at the ammonia oxidation unit.

Travel of the Gas. The burner gas goes to the Glover tower, where it denitrates the mixture of Gay-Lussac acid and water; also it concentrates the acid, carrying the steam into the first chamber, so that in spite of the addition of water at the top of the Glover, the acid issuing from its base is as strong as the Gay-Lussac acid which was fed in. In addition to this steam, exhaust steam or atomized water[4] is admitted into the first chamber right over the inlet pipe, and into the subsequent chamber in a corresponding position. The reaction proceeds vigorously in the first chamber; its intensity is gauged by a thermometer or pyrometer. The steam or sprayed water is regulated so that the specific gravity of the acid is about 55° Bé. To be sure that "newly made" acid is tested, sloping lead tables are built into the chamber with a connecting pipe to the outside, so that the "table drips" may be led, through a seal, to a hydrometer jar.

The gas then passes into the second chamber through a short, wide pipe; then into the third, and so on. In each chamber a heavy mist forms, which slowly settles, leaving the unchanged gases saturated with moisture. The droplets which settle are sulfuric acid containing an amount of dissolved water depending on the amount of steam present. Too little steam causes a strong acid to settle, which on reaching 60° Bé. will dissolve the nitrous acid and form chamber crystals (nitrosyl sulfuric acid, $HNSO_5$). Too much steam may act also to remove nitrous acid by solution in the water of the weak acid, and this will dissolve the lead. The drips indicate in which

[4] It is better to spray in water than to feed steam, but special sprayers are required. Steam is easier to apply; its drawback is that it adds heat to a system which needs cooling.

direction the danger lies. In the last chamber the gas still should be about 2 per cent SO_2 and the temperature 80° F. (27° C.), if the first chamber is 115° F. (46° C.).

Composition of the Burner Gas and Fluctuations. The burner gas should have a composition of 8 to 11 per cent SO_2 by volume for proper working of the chambers. Atmospheric air contains 20.8 per cent oxygen by volume; when using pyrite, 8 volumes are required for the formation of sulfur dioxide, and 3 volumes to form iron oxide; hence there is left 9.8 per cent oxygen on the original volume; when using sulfur, 11 volumes of the oxygen may be used, with none wasted to the cinders, to give 11 per cent SO_2 gas. For the further formation of sulfuric acid, 4 volumes (or 5.5) of oxygen must be provided, plus a slight excess. The nitre gas is furnished by the Gay-Lussac acid diluted by water as it enters the Glover tower, supplemented by enough dry nitre plus Glover acid, or oxidized ammonia, to replace that lost to the atmosphere at the exit from the Gay-Lussac tower. If this normal loss alone were to be made good, the quantity would be constant, say 12 pounds of nitre an hour. But there are irregularities which cause greater losses over short periods. The most interesting of these is the diurnal fluctuation, due to the change in the temperature of the outside air from day to night; and what is more, it does not follow night and day closely, but lags about 6 hours behind. To maintain the proper intensity of reaction, the nitre during the cool period (night) must be decreased, and during the warm period (day) it must be increased. Taking all the causes of loss of nitre gas together, a nitre consumption of 2 to 3 per cent on the sulfur burned for brimstone burning plants is considered normal, and one of 2.5 to 5 per cent for plants running on pyrite and by-product smelter gas.

Aside from general unavoidable irregularities, each set has its own peculiar defects due to its age. Leaks develop through the chamber walls, and to prevent a loss of gas, the fan speed is increased. As a result the gas is leaner, and other guiding temperatures must be settled as being the most advantageous. In other words, each set has its own "best" temperature.

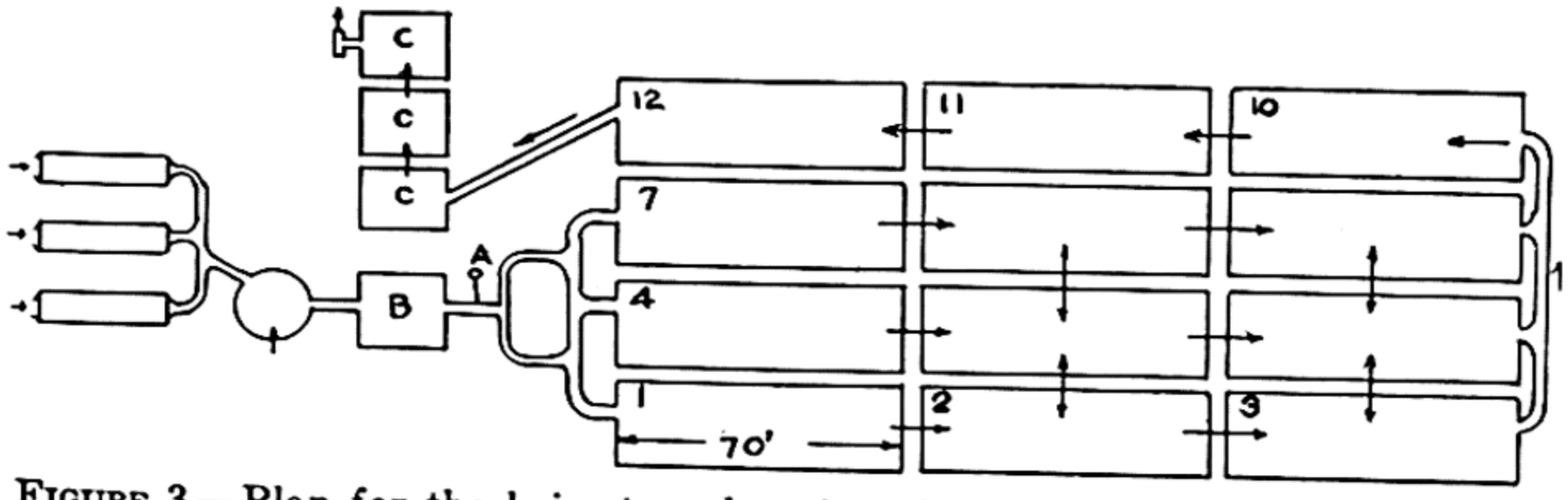


FIGURE 3.—Plan for the brimstone-burning chamber set. *B*, Glover tower, *C*, *C*, *C*, Gay-Lussac tower sections; *A*, ammonia burner.

The set described provides 10.1 cubic feet of chamber space for each pound of sulfur burned per day, if the ore delivers 38 per cent of its weight to the combustion air; this would be an average performance. Sets are compared as to intensity of working by means of this figure; the effort is to make it small.

A chamber plant is very quiet: almost nothing can be heard except the overflow water from the acid cooling tanks.

Brimstone-burning Plant. Another chamber set in which *brimstone* is the source of sulfur dioxide will be described. Its burners are slowly rotating, long, cylindrical steel drums, with the long axis horizontal; the brimstone is melted. A regulated stream of air passes over the sulfur, keeping the blue flame going, and sweeping the combustion gases gently into a com-

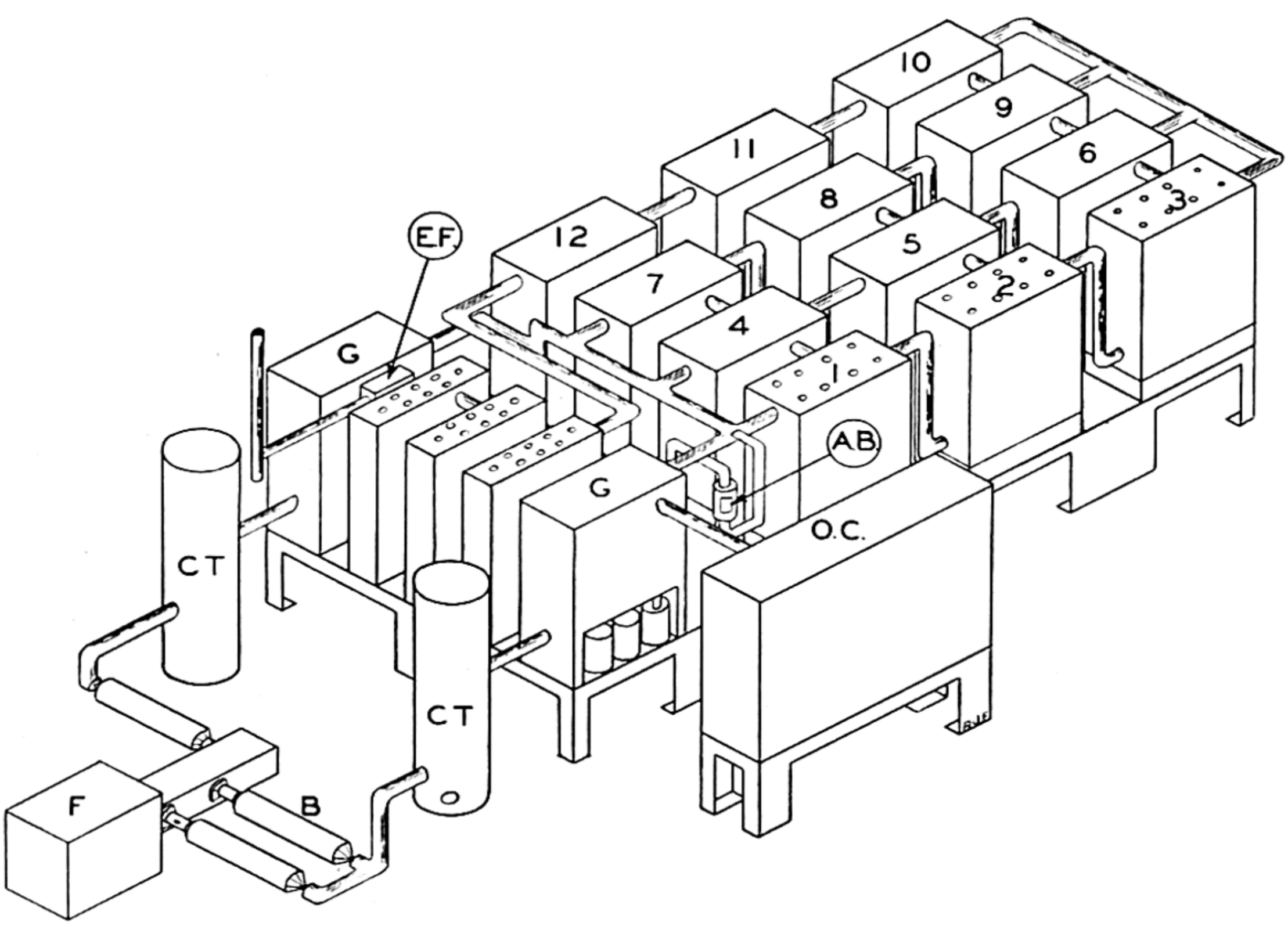


FIGURE 4.—An isometric drawing of a chamber set for sulfuric acid; in a general way but not absolutely to scale. F, sulfur feeder; B, sulfur burner; CT, combustion chamber; G,G, Glover towers; between which are the three sections of the Gay-Lussac tower; AB, ammonia burner; OC, outside chamber; 1 to 12, chambers; EF, exhaust fan. Return pipe from OC to chamber 1 not shown.

bustion chamber, a tall cylindrical brick-lined steel tower set upright, which also receives the combustion gases of two more similar burners. Any entrained sulfur mist is burned here, with the aid of secondary air. The gas testing 11% SO_2 enters the Glover tower; it then receives the nitric oxide from an ammonia burner, and passes into the chambers.

There are 12 chambers, each one 70 feet long, 24 feet wide, and 28 feet high; they are arranged in four groups of three chambers each. The gas enters numbers 1, 4, and 7 from the main header, and travels from each of these through two more chambers before reaching the return header; hence the gas has now swept through 9 chambers. The return header collects the partly reacted gas and sends it all through number 10, from there to number

11, then through number 12, thence to the Gay-Lussac, and finally through the fan to the exit. The operation is more intensive than in the previous set, the temperatures are higher, and the nitre gas loss between 3 and 4%.

The brimstone charge is 3000 pounds per hour; the ammonia burned is 500 pounds of NH_3 per day; the yield is 4.85 pounds of 50° Bé. acid per pounds of sulfur burned, an astounding figure, since the theoretical yield is 4.92 pounds. The space efficiency is 7.83 cubic feet per pound of sulfur burned per day. The temperatures for the first three chambers are 1st, 232° F. [111° C]; 2nd, 232° F. [111° C.]; 3rd, 200° F. [93.3° C.]; in the last three, they are 10th, 180° F. [82 °C.] 11th, 165° F. [73.89° C.]; 12th, 112° F. [44.4° C.]. The Gay-Lussac tower works at 80° F. [26.67° C.];

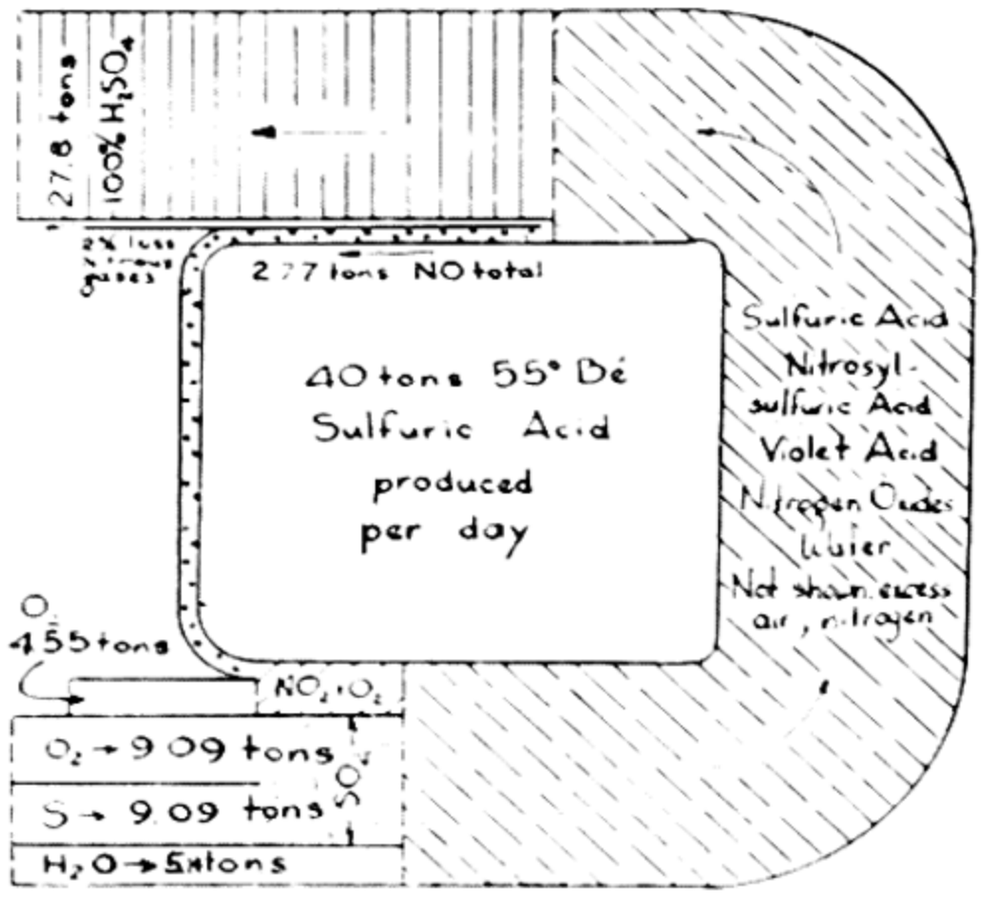


FIGURE 5.—Diagram of materials for a chamber plant which is to produce 40 tons of 55° Bé. sulfuric acid per day. The relations given are the theoretical ones, inasmuch as most plants almost reach these figures. Water of dilution amounting to 12.2 tons is not included in the diagram.

this tower is built in 3 sections standing side by side, the gas traveling up one section, down the second, and up the third. The sections are 20 feet square, and 35 feet in height; the packing is a silica brick. Water is introduced at the top of the Glover, in order to dilute the Gay-Lussac acid and liberate its nitre gas; this is supplemented by water sprayed directly into the chambers, through an atomizer with a porcelain nozzle. Thirty-three per cent of the acid is made in the Glover tower, and 20 per cent in the first chamber; the acid as it leaves the Glover is clear and colorless. All the acid made in the chambers passes through the Glover; the made acid is drawn off from there through coolers, to storage. Such a set runs very smoothly, and the labor requirements are small: one man to bring the sulfur to the hopper feeding the burners, another man for supervision and testing.

Ammonia Oxidation Unit. Numerous ammonia oxidation units have been installed to supply the nitre gas required for the chamber operation.

In such a unit, a mixture of air and ammonia gas (11 per cent NH_3), preheated by the outgoing gases, passes through fine-mesh platinum gauze raised to red heat. At this point, the reaction $4NH_3+5O_2 \rightarrow 4NO+6H_2O$ takes place, with an evolution of 214.2 Calories. This is enough heat so that with proper construction and preheating the gases no heat from an outside source need be applied.

The unit constructed by the Chemical Construction Corporation, is shown in Figure 6.[5] It is designed to receive aqua ammonia, rather than anhydrous ammonia; in the stripper column, warm air removes (strips) NH_3 from the solution; the mixed ammonia and air preheated in the interchanger (7), enter converter (9), where the reaction to form nitric oxide takes place. The outgoing gases reach first the heater (8), wherein the weak aqua ammonia is heated to boiling, then the heat exchanger (7), before

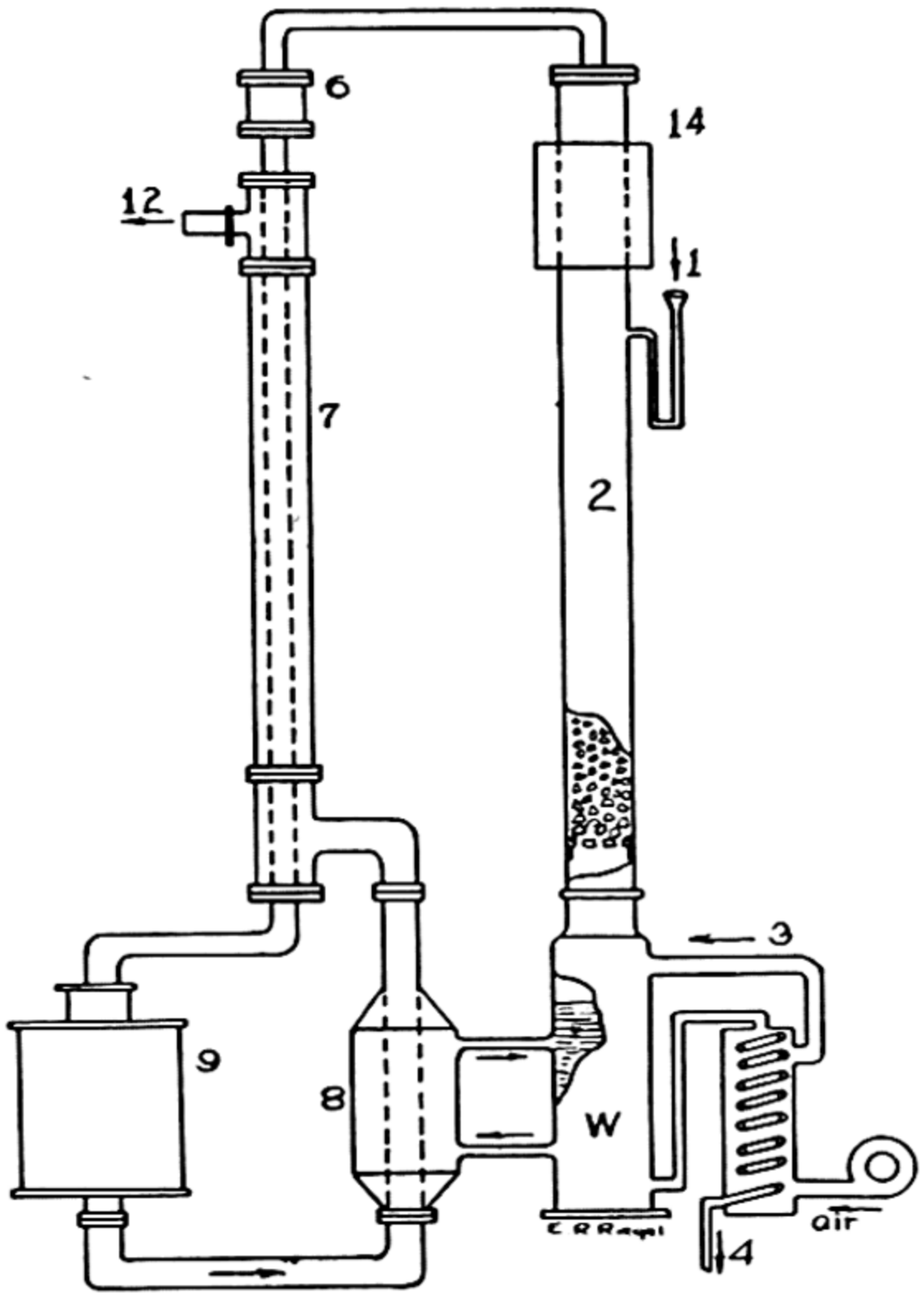


FIGURE 6.—A "Chemico" oxidation unit. 1, entry of ammonia aqua; 2, stripper; 3, warmed air; 4, exhausted liquor to waste; 6, filter; 7, heat exchanger; 8, heater for the ammonia liquor; 9, converter; 12, outlet of nitre gas to the chambers; 14, condenser to hold back excessive moisture. *W*, weak ammonia liquor.

passing out through (12) to the Glover tower. As the gases pass through, an oxidation of the nitric oxide to form a mixture of higher oxides takes place.

A picture of the converter and further discussion of ammonia oxidation are given in Chapter 6, where the manufacture of nitric acid by ammonia oxidation is presented.

Another oxidation unit works on anhydrous ammonia directly.[6] The liquid anhydrous ammonia is vaporized in a coil heated by part of the outgoing gases, passes an oil filter and enters a mixer (a length of aluminum pipe) which also receives the preheated and filtered air required. The mixture, at a temperature of 250° C. [482° F], enters the converter, whose contact material is an 80-mesh gauze of four layers, made of platinum-rhodium alloy (Baker number 750), with strands .003 inch in diameter. At

[5] U. S. Patent 1,748,646.

[6] "Ammonia oxidation makes further gains in chamber plants," Theodore R. Olive, *Chem. Met. Eng.*, 36, 614 (1929).

bright cherry heat, about 900° C. [1652° F.], the conversion is 95 to 96%. A unit burning 24 pounds of NH_3 per hour has a gauze cylinder 4 inches in diameter, and 7 inches high; its life is 6 to 12 months. The warmed anhydrous ammonia gas must pass an expansion valve, which is regulated by a Smoot regulator. The volume of air fed in by a separate blower is filtered at its entry to the blower, and again after it is hot, through a (Mid-West) filter having an oiled filtering surface for the retention of dust particles. The ammonia-air mixture is constantly analyzed and its composition indicated by a Ranarex analyzer (Chapter 46). The operation of the oxidation unit is entirely automatic; the chamber man sights the platinum gauze for color, and reads the Ranarex; adjustments for different poundages to be burned are readily made.

The ammonia oxidation unit working with anhydrous ammonia requires a pressure tank for its storage, for such ammonia is generally bought in tank-car lots. Aqua ammonia requires no special storage provision, which is an important advantage.

The Rotary Burner for Fines. Pyrite fines, the screenings from the lump ore, were at one time waste; the lumps were saleable, but the fines, unavoidably formed in the process of mining and transporting, could not be used because they choked the fire in the lump burner. The fines were disliked also because of the considerable quantity of iron oxide dust which is carried by the combustion gas. They are now burned in automatic rotary shelf burners (*see* Fig. 7) with horizontal shelves and air-cooled raking arms (Herreshoff, Wedge). The spent cinders are discharged continuously from the lowest shelf. With the development of the rotary shelf burners, and of the Howard dust chamber, which permits the fine dust to settle out and thus cleans the gas inexpensively, the fines have became as valuable as the lumps.

The Cottrell electrical precipitator[7] is successfully used for removing iron oxide dust from burner gas.

A method and apparatus for recovering sulfur dioxide from waste ferrous sulfate liquors have been devised.[8]

The treatment of coke oven gas, natural gas and refinery gases by liquid purification processes (*see* Chapter 15) leads to the recovery of vast amounts of hydrogen sulfide, which are now a source of sulfur dioxide for several acid plants.

Flash Combustion Roasting of Iron Pyrite.[9] An entirely new way to burn pyrite, adapted primarily for the very fine powder obtained by the flotation process of treating the ore, has been developed. It consists in feeding the pyrite powder with a small supply of compressed air into a combustion chamber; secondary combustion air comes up from below. The ore burns as powdered coal does. The high temperature of 1000° C. (1832° F.)

[7] Chapter 43.

[8] See flowsheet, *Chem. Met. Eng.*, 42, 699 (1935).

[9] Article by Horace Freeman, *Am. Inst. Chem. Eng.*, 26, 148 (1931); also article by W. M. Cobleigh, *Ind. Eng. Chem.*, 24, 717 (1932), and "Flash roasting of pyrites concentrates in sulphite pulp manufacture," by Horace Freeman, *Chem. Met. Eng.*, 44, 311-313 (1937).

is allowed to develop, to prevent the formation of sulfur trioxide at this stage. Rapid cooling is provided by a fire-tube boiler, followed by a scrubbing tower.

Reactions in the Nitric Oxide-Sulfuric Acid Process

A set of reactions for the nitric oxide-sulfuric acid process has been given[10] by Ernst Berl, formerly a student and co-worker of George Lunge. The following cycle of reactions has been selected from that table; it repre-

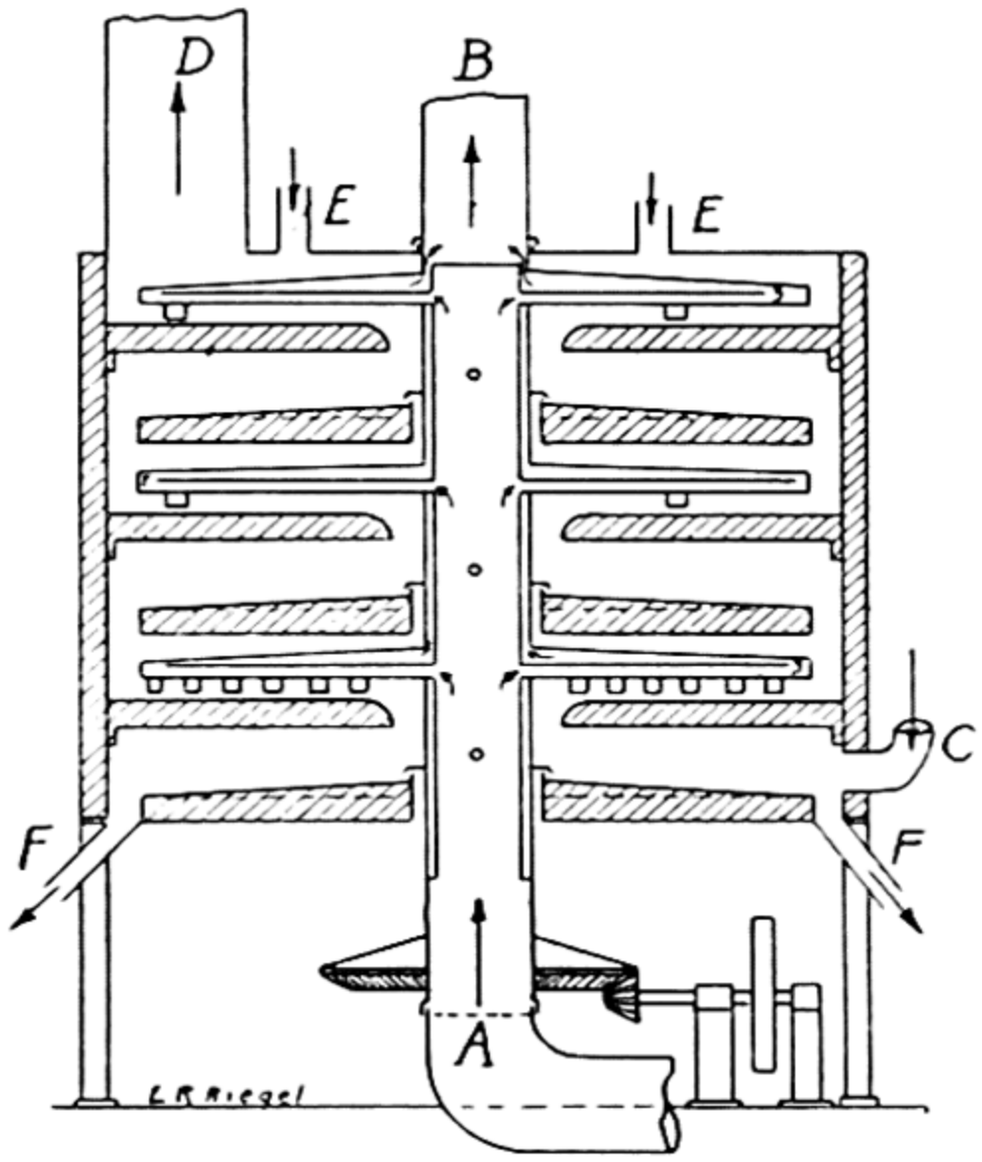


Figure 7.—A rotary shelf burner for fines; *A*, inlet for cooling air; *B*, outlet for cooling air, after it has swept through the rotating arms; *C*, inlet for combustion air; *D*, outlet for sulfur dioxide gas; *E*, inlet for the ore; *F*, outlet for the cinders.

sents the reaction mechanism for the chambers when operated at the usual pressure,[11] that is, one or two inches of water below atmospheric pressure. The reactions explain themselves.

Reaction Mechanism : Sulfuric Acid-Nitric Oxide Process

$SO_2 + \frac{1}{2}O_2 + H_2O \longrightarrow H_2SO_4 + 54$ Cal. Lunge-Berl

1.	$2NO + O_2 \rightarrow 2NO_2$ homogeneous, in the gas phase; trimolecular	
2.	$SO_2 + H_2O \rightarrow H_2SO_3$	heterogeneous, in the gas-liquid surface
3.	$H_2SO_3 + NO_2 \rightarrow (H_2SO_4)NO$ *violet acid*	
4a.	$2(H_2SO_4)NO + \frac{1}{2}O_2(NO_2) \rightarrow 2SO_5NH + H_2O(NO)$ *nitrosyl sulfuric acid*	
5a.	$2SO_5NH + SO_2 + 2H_2O \rightleftarrows 2(H_2SO_4)NO + H_2SO_4$	
4b.	$(H_2SO_4)NO \rightleftarrows H_2SO_4 + NO$	homogeneous, in the liquid phase
5b.	$2SO_5NH + H_2O \rightleftarrows 2H_2SO_4 + NO + NO_2$	
5c.	$SO_5NH + HNO_3 \rightleftarrows H_2SO_4 + 2NO_2(N_2O_4)$	

[10] "Studies of the lead chamber process," Ernst Berl, *Trans. Am. Inst. Chem. Eng.*, 31, 193 (1935); see also *Z. Angew. Chemie*, 44, 291 (1931), Berl and H. H. Saenger; *Z. anorganischen Chemie*, 202, 113 (1931) and 208, 113 (1932), by the same authors; and 208, 124, Berl and K. Winnacker; *Z. Angew. Chemie*, 44, 821 (1932), W. J. Müller.

[11] The theory of Rashig, in which nitrous acid is the working agent, is summarized in the *Journal of the Society of Chemical Industry* for 1911, p. 166. It is now of merely historical interest.

If this process is operated under pressure, the space yield rises; thus there are produced

at 1 atmosphere pressure, 18 lbs of 60° Bé. acid/hour/100 cu ft
at 25 atmospheres pressure, 62,300 lbcs of 60° Bé. acid/hour/100 cu ft

or 3000 times as much. The cycle of reactions[12] for the pressure system, until now not realized in practice, is simpler, and much of the oxidation is

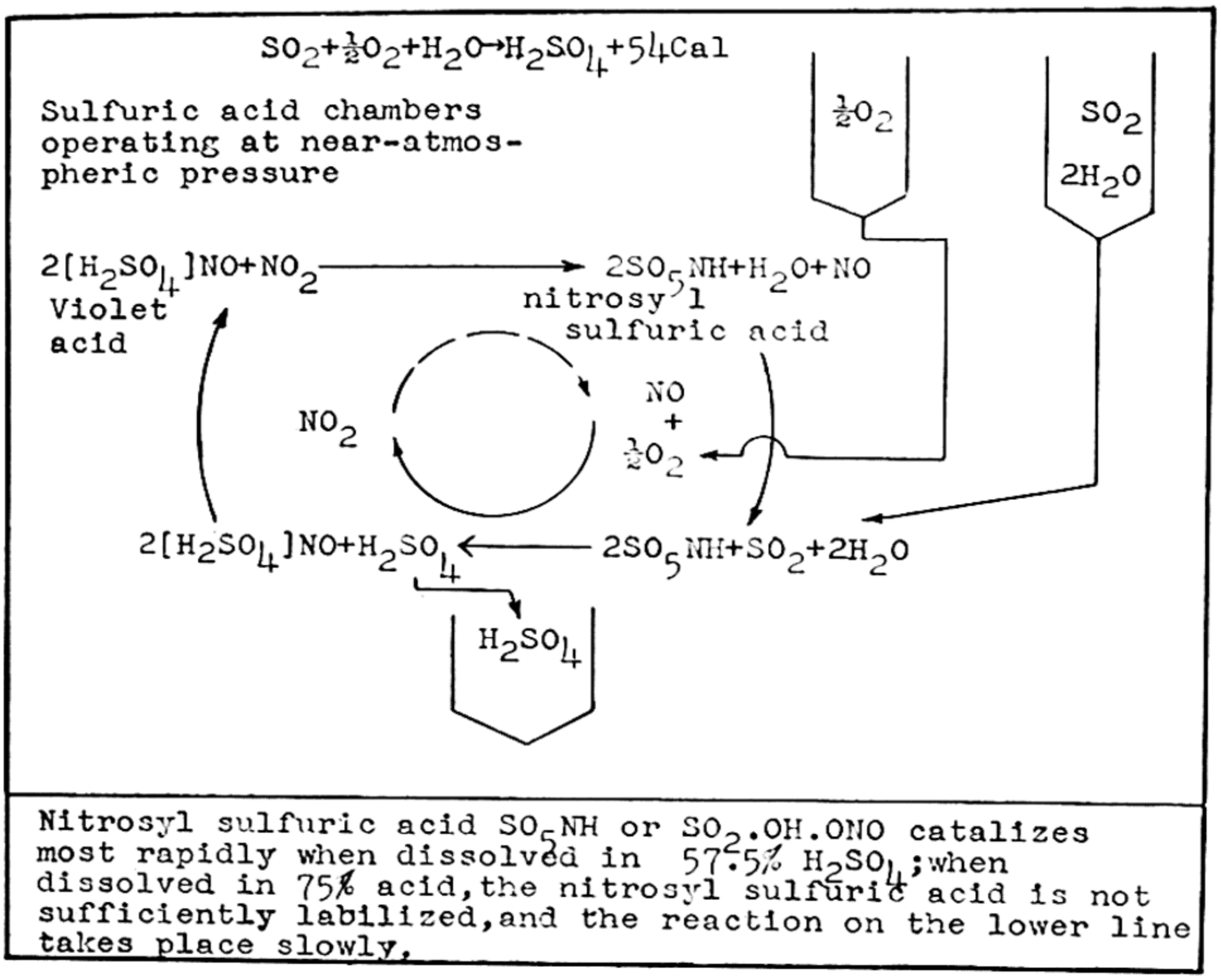


FIGURE 8.—Cycle of reactions in the sulfuric acid chambers, when operating at near-atmospheric pressure.

done by the atmospheric oxygen, so that the Gay-Lussac tower can be small. The pressure may be 10, 25, or 50 atmospheres.

SOURCES OF SULFUR DIOXIDE

The sources of sulfur dioxide are: brimstone, iron pyrite, by-product smelter gas, and hydrogen sulfide recovered from gas purification processes. The lavish use of brimstone is a comparatively new development. Before the war of 1914-18, only 2.2 per cent of the acid was made from brimstone, and that mostly for the production of U.S.P. acid. In the twenties, and since, the amount of sulfur from burned brimstone increased steadily, until in 1941, 69.3 per cent of the total acid was made from it. Of the production of sulfuric acid for the same year, 18.7 per cent came from iron pyrite, 11.4 per cent from by-product smelter gas, and 0.6 per cent from recovered

[12] Given in "Industrial Chemistry," Fourth Edition, p. 27.

hydrogen sulfide. In 1944, the only official figure available is the one for by-product smelter gas, which is 9.6 per cent. It may be estimated that the amount of acid made from brimstone in that year was over 75 per cent, that from pyrite a little more than 10 per cent, and from recovered hydrogen sulfide about 1 per cent. It is likely that more acid from recovered hydrogen sulfide will be made as more recovery plants are installed, using recently improved methods.[13] The greater utilization of recovered sulfur will be welcomed by all friends of conservation of our mineral resources.

Nearly all the states have iron pyrite rock; the production is of importance in New York, Missouri, Colorado, Illinois, and others. Tennessee is the leading producer, if flotation concentrates are included:

TABLE 1.—*Sources of iron pyrite,* in long tons.*

	1940	1944	1945
Domestic production	617,513	788,530	722,596
Imported	407,004	180,763	186,507

* "Minerals Yearbook"

Of the 1944 domestic production, it is estimated that 86,738 tons were lump ore, the balance fines; all analyzed 42.2 per cent sulfur. Pure pyrite, FeS_2, contains 53.4 per cent sulfur. The ore frequently contains arsenic, which is a drawback; less than 0.2 per cent is desirable for the chamber process, and is imperative for the contact process. Pyrite imported from Spain in 1940, the last year of unimpeded importation before the war, amounted to 325,644 tons, and dropped to 14,188 tons in 1944. The Spanish ore serves the plants on the Atlantic seaboard conveniently.

The main source of sulfur dioxide for the manufacture of sulfuric acid is brimstone, the native sulfur. In 1945, there were shipped from the mines for domestic consumption 2,906,962 long tons; it may be estimated that not far from three-fourths of that amount was made into sulfuric acid. Sulfur is mined in Louisiana (783,410 tons in 1945) and in Texas (2,969,778 tons in the same year), by the Frasch superheated water method, described more fully in Chapter 38. Sicily, the most important of the foreign producers, reported a production of 374,339 long tons in 1938, which gradually decreased to a low of 37,000 tons in 1944; in the next year, the production increased to 80,000 tons. In 1944, Chile produced 30,380 tons of sulfur, and in the same year, Mexico produced 29,000 tons of crude sulfur ore.

MODIFICATIONS IN THE CONSTRUCTION OF CHAMBER SETS

Mixing of the gases is essential; this has led to the construction of intermediate towers, of small cubic capacity, placed between the chambers (*see* Figure 1). The towers are packed with stoneware rings.[14]

A great deal of acid is made in the Glover tower—as much as 35 per cent of the total. The conditions in the cooler parts of the tower are propitious: the temperature is high enough, water is abundant, the contact of sulfur

[13] See Chapter 15.

[14] "The manufacture of sulphuric acid in the U. S.," A. E. Wells and D. E. Fogg, Bur. Mines Bull., No. 184, p. 108 (1920).

dioxide, air and nitre gas intimate. This suggested the scheme of providing a second Glover tower, such as the Pratt "converter," at one time highly regarded.

The Anaconda Copper Mining Company has gone a step further: its plant is all towers; there are no chambers. The acid is made in acid-proof brick cells. The cooling is no longer by air, but by chamber acid which passes down the cell towers; this acid is then itself cooled in worms laid in running water, and used over again. The acid made is thus circulated ten times. Per pound of sulfur burned per 24 hours, there is only 1 cubic foot of reaction space.

Of independent conception, there have been erected, in Europe especially, sulfuric acid-nitric oxide plants which also have no chambers, but only towers. The towers are built of acid-proof brick, so that no lead, or very little, is required. Thus a plant may have 2 Glover towers. (4 m diam.×18 m high), 1 production tower (same size), and 4 Gay-Lussac towers (9 m×18 m high).[15] A considerable volume of nitrous vitriol is circulated and recirculated over the Gay-Lussac tower in this type of plant. The nitre supply in sulfuric acid plants, whether of the tower type or chamber type, for various operating rates, may be determined from a formula or from charts.[16]

On the other hand, a sulfuric acid plant which has only chambers, and no towers, has been described.[17] It has a space efficiency of 0.69 cubic foot per pound of sulfur burned per day. The absence of heavy and expensive towers is emphasized, also the relatively low construction cost; in April, 1939, it was estimated that a plant to produce 50 tons of 55° Bé. sulfuric acid per week would cost 5,500 pounds sterling in England.

The Gaillard-Parrish cylindrical sulfuric acid chamber has a turbo-dispenser mounted at the top of the tower-like chamber devised by Parrish. The cooling is by the acid.[18]

Mills-Packard Chambers. In the United States, the Mills-Packard chambers are the most successful of the several newer designs for the chamber process.[19] The new chamber is made of lead, supported by an outside steel frame structure. It is shaped like a truncated cone with the large end down; the dimensions (except for special purposes) are about 27.5 feet diameter at the base, 19 feet diameter at the top, and 50 feet for the height, with a content of about 22,000 cubic feet. The outside walls are cooled by water. The rapid removal of heat promotes the reaction, and in a small space, more sulfur dioxide is oxidized than would be other-

[15] A. M. Fairlie, "Sulfuric Acid Manufacture," p. 215, Reinhold Publ. Corp., N. Y., 1936.

[16] "Determining nitre supply in sulfuric acid plants," P. F. J. Kok, *Chem. Eng.*, p. 127 (Sept. 1946).

[17] "The Watson towerless sulfuric acid plant, a new development in the chamber process," *Ind. Chem. (London)*, p. 159 (April, 1939).

[18] "Liquid phase operation of sulphuric acid chambers gains significance in Europe," *Chem. Met. Eng.*, 36, 68 (1929); also "Thermal aspect of liquid phase sulfuric acid production," *Ibid.*, 37, 93 (1930).

[19] *Trans. Inst. Chem. Eng.* (Brit.) 5, 42 (1927); Brit. Pat. 247,744 and 239,397. *Chem. Met. Eng.*, 37, 468 (1930), and p. 103 (Sept. 1943).

wise, without the water-cooling. Mills-Packard chambers are erected in the open. The set includes Glover and Gay-Lussac towers, and in other ways, it is operated like the chamber sets with box chambers.

Many improvements in construction have been made. The cooling water travels down without interruption from the top to the bottom trough, which has been lowered so that the acid collected in the pan may also be cooled. The lead walls are supported by vertical lead straps, each strengthened by two flat iron bars, bolted one on each side of the strap. The latter is bolted at intervals to an angle ring, part of the supporting steel structure, through an eye-bolt and ring, permitting a certain degree of expansion and contraction of the wall without strain.

The many ways in which the Mills-Packard chamber can serve is indicated by the following installations made during the past four years: "Five new M.P. plants have been built; five box chamber plants have been rebuilt replacing worn-out box chambers by Mills-Packard; single Mills-Packard

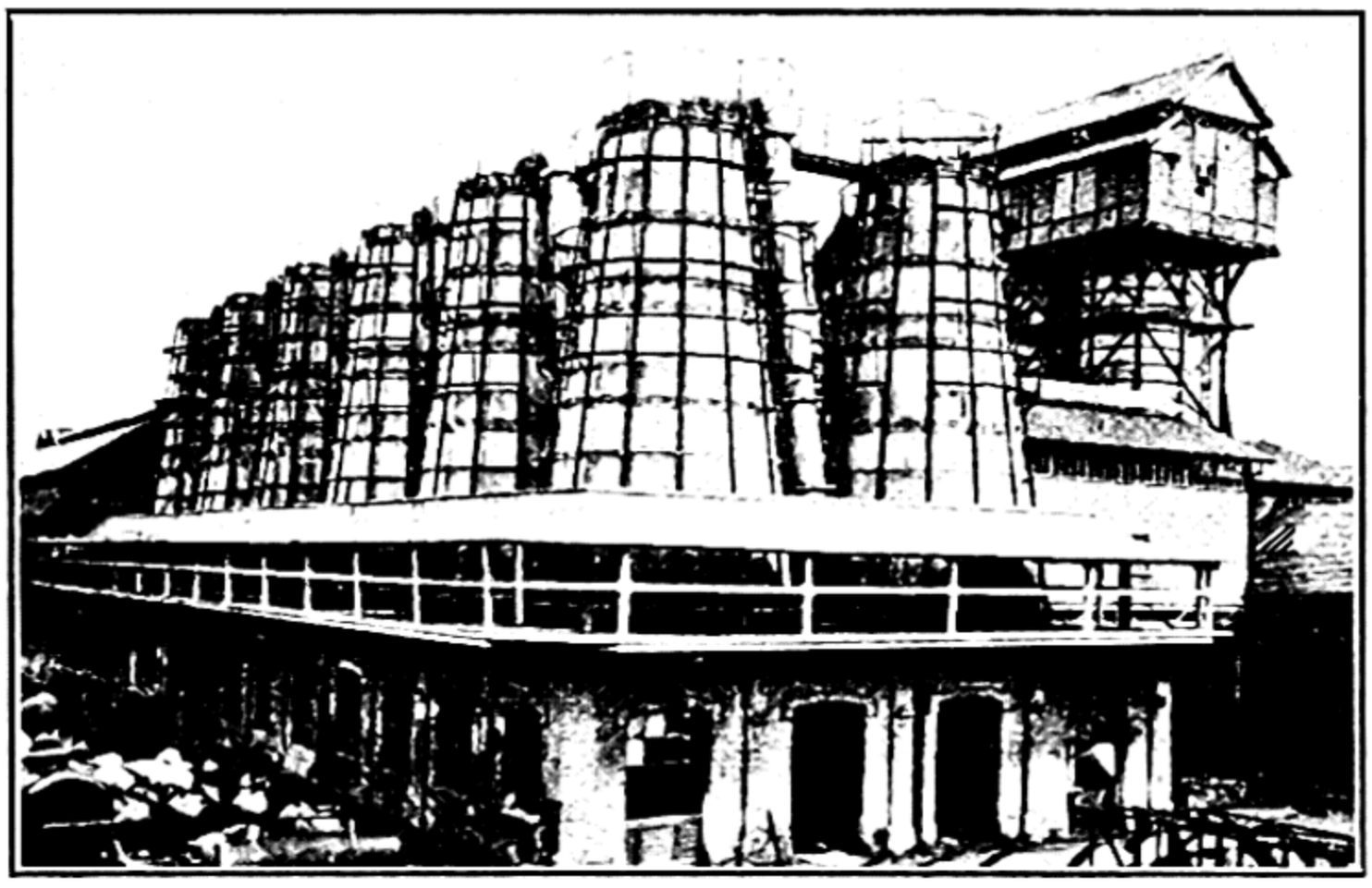


FIGURE 9.—Twelve Mills-Packard sulfuric acid chambers, truncated cone-shaped outside water-cooled, free from enclosing structures; the Gay-Lussac and Glover towers are to the right. (Courtesy of Mr. Andrew M. Fairlie, Chemical Engineer, Atlanta, Ga.)

chambers to replace single box chambers have been erected at two plants; additional M.P. chambers for increasing the capacity of existing box chamber plants have been built at three plants, a total of 49 new Mills-Packard with an aggregate daily capacity of 784 tons of acid, at 15 different plants, in the United States, since January, 1944. Besides these, a 4-chamber M.P. plant was erected in Brazil in 1944-45, and a 40-ton M.P. plant is now being designed for erection in South Africa."[20]

All these constructions were made in spite of the high price of lead, about 17½ cents a pound, compared with the pre-war price of, let us say, 6 cents. The chamber process is still far from obsolete. For the production of 60° Bé. acid, the chamber process has the following features to recommend it: Compared with the contact process, the operating costs per ton of 60° Bé. acid are lower, as are generally also the depreciation and maintenance costs; there is no extra expense for diluting high-strength acid; there is no need for boilers nor the expense items which go with them. The Mills-

[20] Private communication from Mr. Andrew M. Fairlie, Consulting Chemical Engineer, Atlanta 1, Georgia.

Packard chamber process is the most flexible type of sulfuric acid plant as to production capacity, inasmuch as it is capable of a range from about 40 per cent of rated capacity (by leaving out the cooling water on the chambers), to 120 per cent of rated capacity, with cooling water, and forced operation methods.

A comparison of the efficiency of the more important chamber systems is given below.

TABLE 2.—*Efficiency of sulfuric acid chambers system in terms of space.*

Chambers	Cubic feet of space per pound of brimstone burned per 24 hours (annual averages)	Cooled by
Rectangular	7.5-10.0	air
Mills-Packard	2.5- 3.00	water
Gaillard-Parrish	2.5- 3.0	cold-acid circulation
Anaconda cells	1.0 (approx.)	cold-acid circulation

FIGURE 10. — A Mills-Packard chamber plant.

Two other processes deserve mention, although neither is in successful operation at the present time in the U.S.; they are the Schmiedel process,[21] in which nitrosyl sulfuric acid is sprayed into the sulfur dioxide gas to provide as great a contact as possible; and the pressure process, designed for a 4-ton per day production,[22] in which sulfur gas is introduced into a sealed tower 18 inches in diameter, which replaces the chambers.

Concentration. The chamber acid may be concentrated without expense for fuel from its normal strength of 53° to 60° Bé. by passing it through the Glover tower. It may be concentrated to the still more valuable 66° Bé. acid with the aid of coal or oil fire, as described in part II of this chapter. It is not possible to concentrate chamber acid above 97 per cent by heat, because above such strength the acid decomposes.

[21] U. S. Patents 1,399,526 and 1,512,863.
[22] U. S. Pat. 1,513,903.

In addition to production figures given in the introduction to this part of the chapter, it might be said that 1946 production dropped to 8,649,163 short tons of 100 per cent acid, but 1947 production is estimated at 9,900,000 tons, for both chamber and contact acid combined.

Prices. The prices of raw materials vary with market conditions, and for other reasons. The price of the product varies also, depending upon market conditions, length of contract, and specifications. The figures below are intended merely to indicate the usual price range.

In 1945, domestic iron pyrite brought $8.73 a long ton; its sulfur content was 41.0 per cent. The sulfur it contained cost, therefore, 0.407 cent per pound, equivalent to $8.95 a long ton. The price of imported pyrites at Atlantic ports in 1944 and 1945 was 14 cents a unit. (One per cent by weight of sulfur in a long ton is one unit.) Brimstone, which was sold at $16 a ton, costs then 0.73 cent a pound. Brimstone as raw sulfur is now $16 and $18 per long ton, at the mines.

Sulfuric acid, 60° Bé. is quoted currently at $12.50 a ton in carload lots.

Anhydrous ammonia is quoted currently (April, 1948) at $59 to $70 a ton, in car tanks. The $59 per ton figure is equivalent to just under 3 cents a pound.

The cost of erection of a standard chamber plant was estimated at $2,100 to $3,000 per ton of 60° Bé. acid produced per day, prior to 1940.

Problems

1. In the brimstone-burning chamber plant described in the text, the number and dimensions of the chambers are given, as well as the pounds of sulfur burned per hour. Compute the total chamber space available; extend the weight of sulfur burned to 24 hours, and find the space efficiency figure, then compare it with the figure in the text.

2. Find the pounds of 50° Bé. acid which may be made from 1 pound of sulfur. What is the percentage yield, if for each pound of sulfur, 4.60 pounds of acid are made?

3. Find the weight of water which must be furnished per day for the amount of acid made per day in the brimstone-burning set.

4. In the same set, if the nitric gas loss is 3 per cent of total nitric oxide in the set, including the Gay-Lussac acid, what is the total nitric oxide present?

5. Burning a pound of NH_3 to nitric oxide is equivalent to potting how many pounds of sodium nitrate, 100 per cent pure? Check the figure given in the text.

6. In the burner house, six burners of the rotating type receive 1000 pounds of brimstone each, every hour. The gas passes to 14 Mills-Packard chambers. How closely will the resulting space efficiency figure agree with the figure given in the table in the text, for such chambers?

7. Set up factors for changing sulfur, by weight, to H_2SO_4 100 per cent by weight, to 66° Bé. sulfuric acid, to 60° Bé., to 55° Bé., to 50° Bé. sulfuric acid. The percentages of H_2SO_4 for the several strengths will be found in the texts.

8. Let the volume of gas from the burners be 8 per cent SO_2. In the first set described, in which the sulfur delivered to the gas is $30 \times 1000 \times 0.38$ per day, what is the weight of the sulfur equivalent, and of the sulfur dioxide produced, in pounds? What is the volume of the resulting 8 per cent SO_2 gas? The gram mole and the gram molecular volume in liters may be used, with a conversion figure taken from the appendix. For this purpose, assume that the gas is at STP. Let the 8 per cent gas be delivered through a 36-inch diameter line to the system; what is its velocity, in feet per second? To find it, compute the volume of 8 per cent gas served per second. If the gas has a temperature of 200° F. [93.3° C.] when passing through the 36-inch line, what is its velocity?

9. What is the cost of materials for making 40 tons of 50° Bé. sulfuric acid per day, by burning brimstone, when the latter is bought at $16.00 a ton of 2240 pounds, plus 1 per cent for freight? The water is free.

10. The roof and the sides of the chambers are made of seven-pound lead, that is, of sheet lead weighing seven pounds to the square foot; the bottom is 10-pound lead. For the set of 12 chambers of the brimstone-burning plant, what is the weight of the lead required, and what is its cost, if the sheets as delivered are 6.5 cents a pound? An additional amount will be needed for the Gay-Lussac tower, for the Glover, and for the cooling tanks and their cooling coils at the foot of the Glover.

The difficult step in the manufacture of sulfuric acid by any process is the change of sulfur dioxide to sulfur trioxide. If sulfur burned to form the trioxide at once, there would have been no opportunity for the many fine minds of chemists and chemical engineers to display their inventiveness and ingenuity; but it burns to the dioxide only, and it needs help to get over the hump to the higher oxide. In the chamber process, this help comes from the gaseous oxides of nitrogen. In the contact process, the assisting agent is a solid; in contact with its surfaces, at the proper temperature and concentration, the reactants unite to form the desired trioxide. In the older literature, there are many papers which deal with the "wall' effect; these studies and observations have culminated in the contact substance.

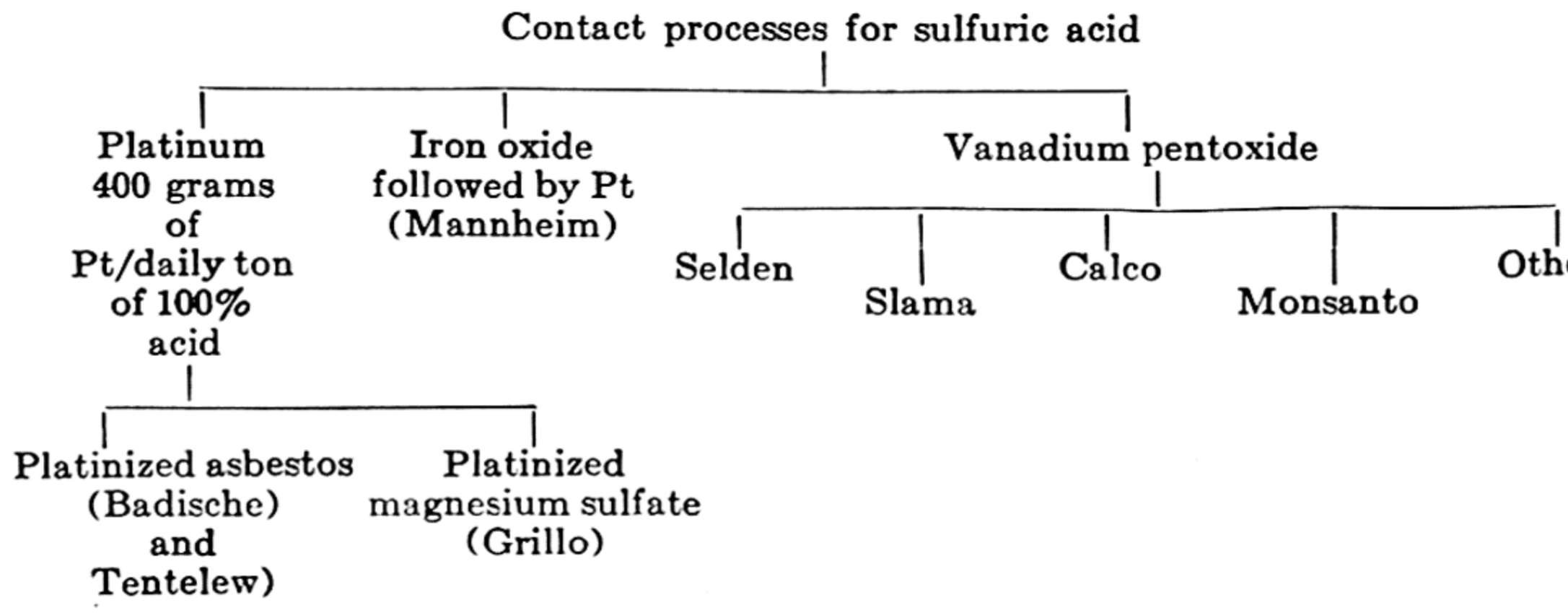
Chapter 1—(Continued)

Sulfuric Acid—Part II: The Contact Process

The contact method became a firmly established industrial process at the turn of the century. Until about twenty years ago, the contact material usually was finely divided platinum on a carrier of either asbestos or calcined magnesium sulfate. Iron oxide, which was also used in the early years, was of secondary importance. The situation has changed entirely since 1926, when the introduction of vanadium pentoxide as the contact substance took place in the United States.[1] This less expensive agent is not used as such, but is always supported on an inert carrier, such as diatomaceous earth, which does not melt or soften at the high temperatures employed [around 450° C. (842° F.)]. Its service has been so satisfactory that new installations are designed for the use of the vanadium catalyst, and the older installations, when replacement becomes necessary, will be redesigned for the new contact substance instead of platinum.

The contact process is so called because the reacting molecules meet in contact with the walls of the solid catalyst, which may also be the walls of pores and micropores in the agent provided.

The several processes may be grouped as follows:



[1] Vanadium catalysts were in use in Europe during the war of 1914-18 in special installations; they came into general industrial use in Europe in 1921.

Jammu & Kashmir University Library
Accession No. 49895

The low platinum mass, mainly as platinized silica gel, is no longer used. It contained 62.2 grams of platinum per ton of 100 per cent acid.

All the contact processes form sulfur trioxide, the anhydride of sulfuric acid. It is a gas at any temperature above 45° C (113° F.) and at atmospheric pressure.

On distilling sulfuric anhydride and condensing the vapors above 27° C. (80.6° F.), there is formed a liquid, the γ-form of SO_3, which solidifies to an ice-like solid having a melting point of 17° C. (62.6° F.). The γ-form melts easily and readily, and boils at 45° C. (113° F.). In moist air, the boiling liquid smokes furiously. If the condensation of the same vapors takes place under the influence of moisture and below 27° C. (80.6° F.), the sulfur trioxide vapors condense to form not only the γ-form, but also the β-form, a polymer, and a third form, the α-form, a higher polymer; the latter two are asbestos-like solids, more difficult and sometimes dangerous to melt. In water, sulfur trioxide dissolves explosively, but in sulfuric acid of 98 per cent strength, it dissolves smoothly and quietly, and this acid is the common absorbent.

The contact process yields sulfuric acid of any strength up to 100 per cent H_2SO_4; beyond that it is made in the form of oleums which contain the anhydride SO_3 in solution. Oleums have been available in several strengths, up to 65 per cent free SO_3, for many years. Just recently, a new material with 100 per cent SO_3, has been placed on the market under the name of "Sulfan" (see further). Oleums serve for certain sulfonations which sulfuric acids fail to bring about, but one of their important functions is to fortify weaker acids to the strength required.

The reaction $2SO_2 + O_2 \rightarrow 2SO_3$, which takes place in the converter (under proper working conditions), runs to 97 per cent completion at a temperature of about 450° C. (842° F.). The catalyst may be platinum,[2] vanadium pentoxide, or iron oxide. At temperatures appreciably below 450° C. (842° F.), sulfur dioxide escapes oxidation. At somewhat higher temperatures, the opposite reaction, $2SO_3 \rightarrow 2SO_2 + O_2$, takes place; the result in either case is the same, namely, the conversion falls below 97 per cent. The conversion figure is obtained by dividing the sulfur dioxide which is oxidized by the sulfur dioxide fed into the converter, and multiplying by 100. On closer examination, it is found that the rate of reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is only moderate at 400° C. (752° F.), but increases enormously with a rise in temperature. Thus at 500° C. (932° F.) it is 40 times as great as at 400° C. (752°F.). By rate of reaction is meant the amount of sulfur dioxide converted in unit time. The opposite reaction, $2SO_3 \rightarrow 2SO_2 + O_2$, is also accelerated by a rise in temperature, but becomes appreciable only at much higher temperatures. For example, at 400° C. (752° F.) it hardly takes place at all; but at 550° C. (1022° F.), its rate is high enough to produce a fair amount of the lower oxide. Hence it would be advantageous to provide a temperature of 550° C. (1022° F.) to the gas as it enters the catalyst

[2] The honor of having discovered that platinum catalyzed the reaction to form the trioxide belongs to Peregrine Phillips, Jr., of Bristol, England (1831). Platinized asbestos was proposed first by the Englishman Jullion (1846).

mass, and then after 80 per cent conversion or so, to cool the gas gradually, so that as it sweeps through the last portions of the mass, the temperature would be 425° C. (797° F.). In this way a rapid reaction, and at the same time a high conversion, should be attained.

The oxidation reaction is exothermic: $2SO_2+O_2 \rightarrow 2SO_3+45.2$ Calories. This heat must be dissipated in the proper degree to prevent excessive temperatures which would cause the reverse reaction $2SO_3 \rightleftarrows 2SO_2+O_2$ to proceed vigorously. More than enough heat is generated to maintain the apparatus at the proper temperature, and to preheat the incoming gases.

The catalytic reaction $2SO_2+O_2 \rightleftarrows 2SO_3$ is reversible. It is desirable to drive it to the right. The law of concentration effect (the mass law) requires that the concentration of one of the factors (SO_2 or O_2) be increased, if it is desired to increase the formation of the product. By increasing the concentration of the oxygen, more of the product is formed, while at the same time, the sulfur dioxide is nearly exhausted.[3] The burner gas contains 8 per cent SO_2 which would require only 4 per cent O_2 for the reaction as written; but 10 per cent or more is always provided, an excess of over 150 per cent, thus insuring a high conversion figure.

The conversion depends furthermore upon the temperature, the period of contact, that is, the relation between volume of mass and cubic feet of gas,

[3] At any one definite temperature within the range concerned, and in the presence of the catalyst, an equilibrium between the gases SO_2, O_2 and SO_3 will be attained, provided enough time is allowed. The value for the equilibrium constant in the formula

$$K_p=\frac{(PSO_3)}{(PSO_2)(PO_2)^{\frac{1}{2}}}$$

using partial pressures in atmospheres, for the temperatures observed in practice, is:

Temperature	K_p	K_c
400° C.	467	109,700
425	255	61,000
450	145	35,300

Expressing the constant in terms of mols per cc., for the same reaction, the values listed under K_c are obtained.

The reader will please note that the expression applies to the reaction $SO_2+\frac{1}{2}O_2 \rightarrow SO_3$, not for the reverse reaction, nor for the reaction written with twice the number of molecules; for the latter the value of the constant will be the square of the above values; for the former, the reciprocal.

It may be well to point out that it is the constant K which does not change, while the absolute amounts of the three gases may be altered. If the concentration of oxygen is increased, the value of (PSO_2) must decrease, to maintain the value of K, assuming the change in (PSO_3) to be relatively small. This is what happens when a 100 or 200 per cent excess oxygen is provided. K may also be expressed in terms of the constants of the reaction rate, k_1 for the forward reaction, k_2 for the reverse reaction, then $K=\frac{k_2}{k_1}$.

The earliest researches on the value of the equilibrium constant, specific rate constant, and optimum temperature were those of Knietsch, which formed the basis for the original contact process with platinum, the "Badische" process. A summary will be found in *Berichte der deutschen chemischen Gesellschaft*, v. 34, p. 4093 (1901). Knietsch used flowing gases; more recently W. K. Lewis also used flowing gases, and reconsidered Knietsch's data as well as set up new values by experiments: "Influence of reaction rate on operating conditions in contact sulfuric acid manufacture," *Ind. Eng. Chem.*, 19, 830 (1927) and 17, 593 (1925), where references to the work of Bodenstein on quiescent gases will be found. See also "reading references."

and upon the activity of the mass. The pressure on the gases is essentially atmospheric pressure.[4] The commercial installations illustrate all these factors.

The function of the contact substance is to adsorb the reacting gases at its surface; in the closer proximity which results, coupled with the high activation caused by the high temperature, the successful collisions are enormously increased in number, and the speed of reaction is correspondingly raised. In the case of platinum, surface adsorption is the only function. For vanadium pentoxide (or other oxides), it is more likely that the various oxides of vanadium do take part in the action; the higher oxides give up oxygen, but are continually reformed by the incoming oxygen, so that they are found unchanged after the reaction. It may be said, therefore, that the contact substance in any process is unchanged after a period of years. Commonly, the life of a mass is considered to be 10 years. The subject of poisoning will be presented after the plants have been described.

Additional discussion of catalytic reactions will be found in Chapter 25.

The Chemico Process with Vanadium Mass

A Chemico contact sulfuric acid plant of capacity of 17 tons 100 per cent H_2SO_4 a day will be described as typical of the most advanced practice of the present period. The plant is built entirely of iron and steel with some acid-proof masonry and ceramic packing in the drying and absorption towers. It has many features which will be welcomed by the student, particularly two: simplicity and compactness. The simplicity of the plant results largely from the use of brimstone sulfur as raw material; all auxiliary apparatus for cleaning burner gas from the combustion of pyrite is absent. Sulfur is melted, burned with air in the special spray burner; the combustion gases, with 7 or 8 per cent SO_2, are cooled by passing them through a waste heat boiler, and then enter the converter. However, one important purification is provided: the air is dried. The drying avoids a number of difficulties, such as corrosion of parts and mist formation. The *compactness* of the plant is such that it is housed complete in what might be a good-sized room.

The diagrammatic flow-sheet in Figure 11, drawn from an actual plant, gives the sequence of operations. Melted sulfur is forced through the spray burner tip by a steam-driven turbine, submerged in the sulfur. The pressure on the melted sulfur is sufficient to drive it through a spiral cut in the

[4] The reaction $2SO_2 + O_2 \rightarrow 2SO_3$ involves a decrease in volume, from 3 to 2, and one would expect that by running the process at a higher pressure, the rate of reaction would be accelerated, and the amount of material would be greater for a given space and contact mass. Yet, as far as is known, all contact processes are run at near-atmospheric pressure, although proposals for, and trials at higher pressures have been made. The explanation probably lies in the slowness of one of the steps, of which the simple reaction given above is but a summation. The rate of diffusion of the incoming sulfur dioxide and oxygen mix to the surface of the catalyst is the slowest step, and it is this step which sets the pace for the reaction as a whole. The sulfur trioxide is strongly adsorbed on the surface of the catalyst, and it is through this layer of adsorbed sulfur trioxide that the incoming gases must diffuse. Increase in pressure would perhaps raise slightly the speed with which sulfur dioxide and oxygen travel through the sulfur trioxide layer, but the thickness of the latter would probably be increased, thus nullifying the first beneficient effect. [See Discussion by Dr. J. H. Perry of the paper by Dr. Ernst Berl, *Trans. Am. Inst. Chem. Eng.*, 31, 223 (1935).]

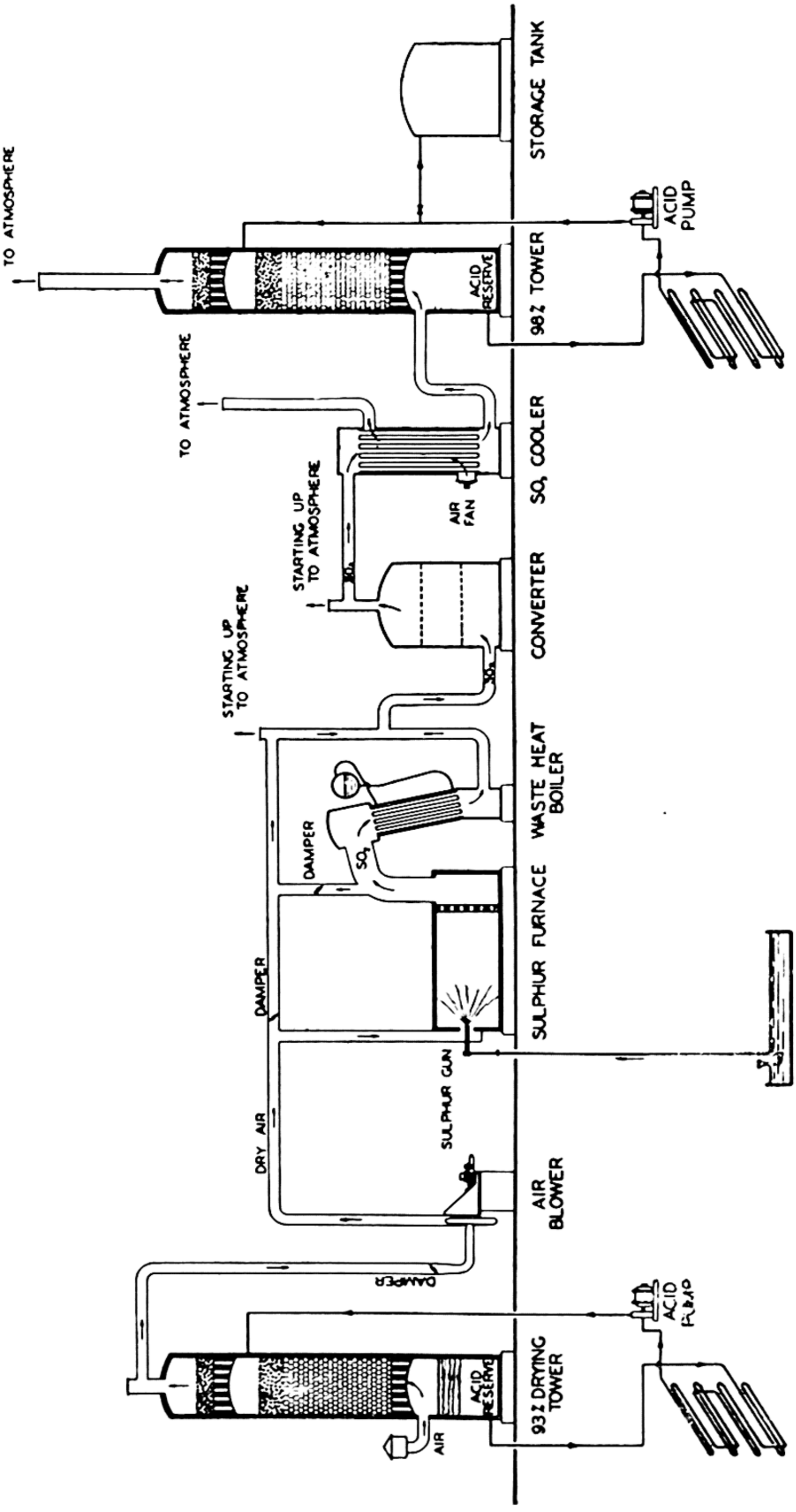


FIGURE 11.—Diagrammatic flow-sheet for the "Chemico" sulfuric acid contact process using brimstone as source of sulfur, latest design. The air for the combustion is dried in a single tower, and served to the burner on the pressure side of the fan. The sulfur trioxide is absorbed in a single tower to give 98 per cent acid. When oleum is desired, two towers are erected, the first for oleum, the second for 98 per cent acid. (Courtesy of the Chemical Construction Corporation, New York.)

adjustable valve rod (needle-valve type), so that it acquires a rotary motion and is discharged into the burner in a wide arc. Air is drawn upward through a packed steel tower, down which a heavy stream of cold 93 per cent sulfuric acid flows. The acid is circulated by a pump and is cooled by traveling through cast-iron cooling pipes laid in water. The dried air passes through a centrifugal blower and is delivered under forced draft to the sulfur furnace. The chamber for burning 5 (or 6) tons of sulfur per day is a cylinder lying on its side, 7 feet high and 17 feet long. It is of steel, brick-lined, with a terminal baffle. The gases leave the burner at 771° C. (1490° F.), and pass through a boiler, the tubes of which are surrounded with water. The steam

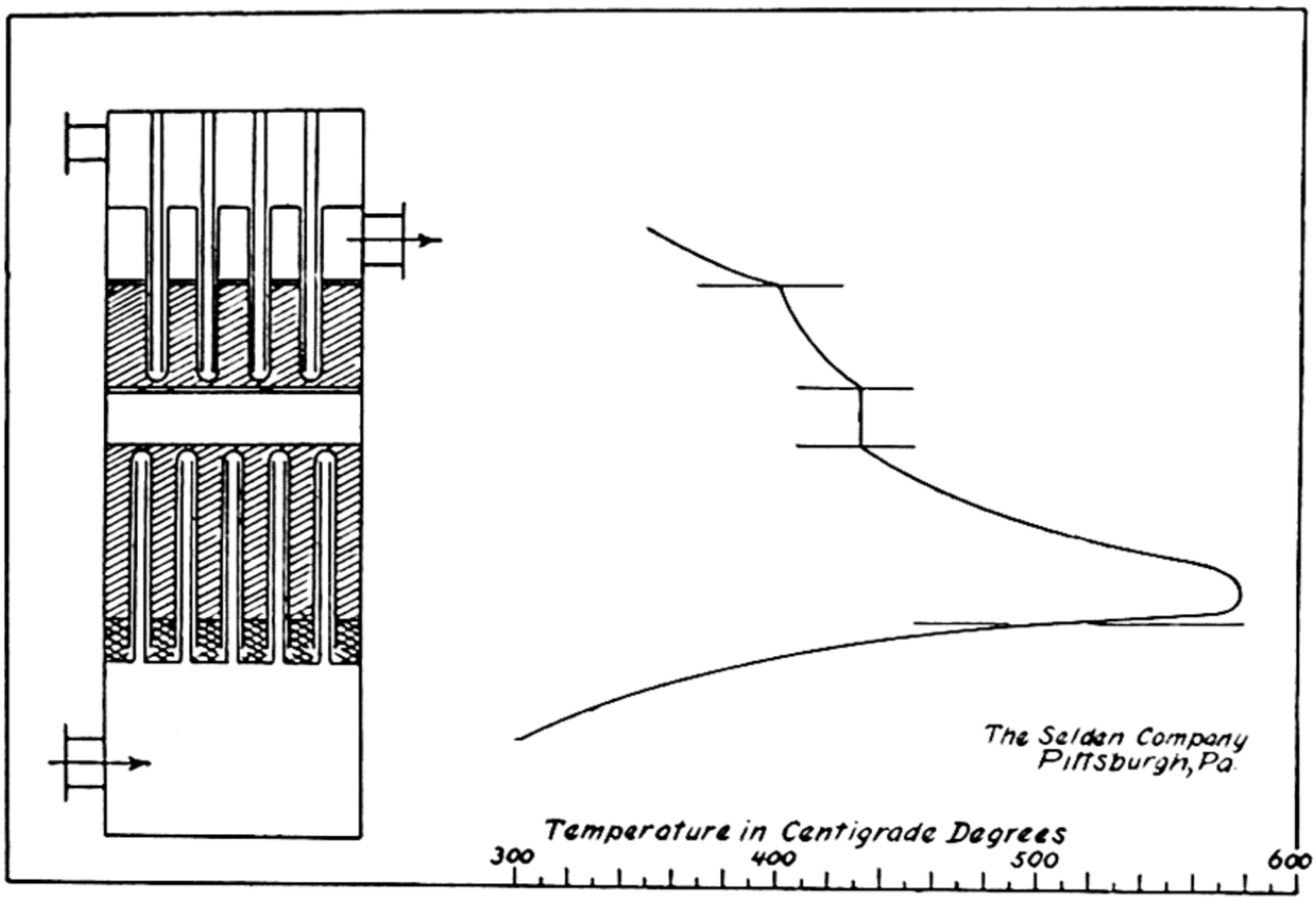


FIGURE 12.—The temperature for gas and mass at various levels in the "Selden" vanadium pentoxide packed converter for sulfur trioxide formation.

generated is sufficient to melt the sulfur, run the steam turbine which runs the sulfur pump, and drive the main blower. By-pass flues around the furnace and waste heat boiler permit the regulation of the SO_2 concentration and the temperature of the gas entering the converter.

On leaving the boiler, the gases, with temperature 304° C. (580° F.), enter the converter, which carries the contact mass in two layers: 1800 pounds in the lower layer, 1200 pounds in the upper. One pound of the catalyst occupies one liter volume. The internal arrangements for the earlier models are as shown in Figure 12, which also gives the temperature for the gas (and mass) at various levels. The lower layer is cooled by the entering gases which reach the top of the risers, and are deflected downward by means of the slender thimbles inverted over them. In the upper layer, the mass is cooled by a current of cold air. In later forms of the converter, internal risers and thimbles are dispensed with, greatly simplifying the construction; an outside heat transferrer is used for the heat exchange.

On entering the bottom mass, the gases are at 493° C. (920° F.); 6 inches above the lowest layer is the maximum temperature 593° C. (1100° F.). On leaving the bottom mass (upper portion) the gas is at 482° C. (900° F.); the temperature in the top layer, where the conversion is completed, is 438° C. (820° F.).

The hot sulfur trioxide gas produced is cooled in a tubular heat exchanger by a stream of cold air from a fan, and is absorbed in a 98 per cent sulfuric acid tower. The latter is built of masonry, and filled with a checker-work of acid-proof bricks preceded by baffles, and surmounted by a bed of pebbles; a second level of baffles and pebbles insures mixing of the gas and good contact with the descending acid, so that the gas passing to the atmosphere through a stack is exhausted. The absorbing acid is diluted continuously by means of a weaker acid, such as chamber acid, or by means of water, in amount sufficient to keep the strength about 98 per cent. A heavy stream of absorbing acid is maintained, and its heat is continuously removed by passing through cooling pipes laid in water. The made acid is collected in a storage tank and transferred from there as needed. The waste gas, consisting of nitrogen, oxygen, and any unchanged sulfur dioxide, leaves at the top of the tower.

When oleum is to be made, the oleum tower precedes the 98 per cent acid tower, and receives the gas first. The strength of the oleum is controlled by regulating the amount of acid fed to it; the stronger the oleum required, the slower the stream of acid. The gas leaving the oleum tower is still high in SO_3 content, and passes to the 98 per cent acid tower, where complete absorption takes place. The oleum leaving the oleum tower is collected separately, adjusted for strength if necessary, and pumped to storage or shipping tanks.

In a larger plant, built during the recent war and designed to produce 200 tons of acid every day, expressed as 100 per cent H_2SO_4, the first converter contains 40 per cent of the catalyst, the second 60 per cent. The converters are of the tray type, illustrated in Figure 13. The sulfur gas enters the primary converter at 425° C, and leaves, with 78 per cent conversion, at 595° C. After cooling in the heat exchanger, the gas enters the secondary converter at 425° C., and leaves at 455° C. In another exchanger, the temperature of the exit gas, now 97 per cent SO_3, is reduced to 240° C., and it is sent at that temperature to the absorber for making 98 per cent acid. In order to make oleum, it is first cooled further.

The acids are recirculated by means of special metal LaBour motor-driven pumps (Chapter 41).

Oleums. Oleums are made in a number of strengths, such as 15, 20, 40, 60 and 65 per cent free SO_3 by weight. Their freezing points vary considerably (see Figure 17) and must be taken into account. The pure substance itself, as stated early in the chapter, is a white solid, which in itself presents no unexpected difficulties in handling; unfortunately, it polymerizes to a fibrous solid which on being heated melts with great difficulty, and mainly sublimes.

"Sulfan." As previously mentioned, there has recently been placed on the market,[5] a 100 per cent oleum, better called a stabilized sulfuric anhydride, which presents none of the difficulties mentioned. In this form, it is a liquid and remains one, thanks to the introduction of a stabilizing agent (0.25 per cent). This new material is available in drum lots, and soon will be available in tank-car lots. The stabilized sulfuric anhydride, called "Sulfan," is made in the oleum tower and collected warm; only a portion of the sulfur trioxide gas is condensed for this purpose, the rest passing to the regular 98 per cent sulfuric acid absorbing tower.

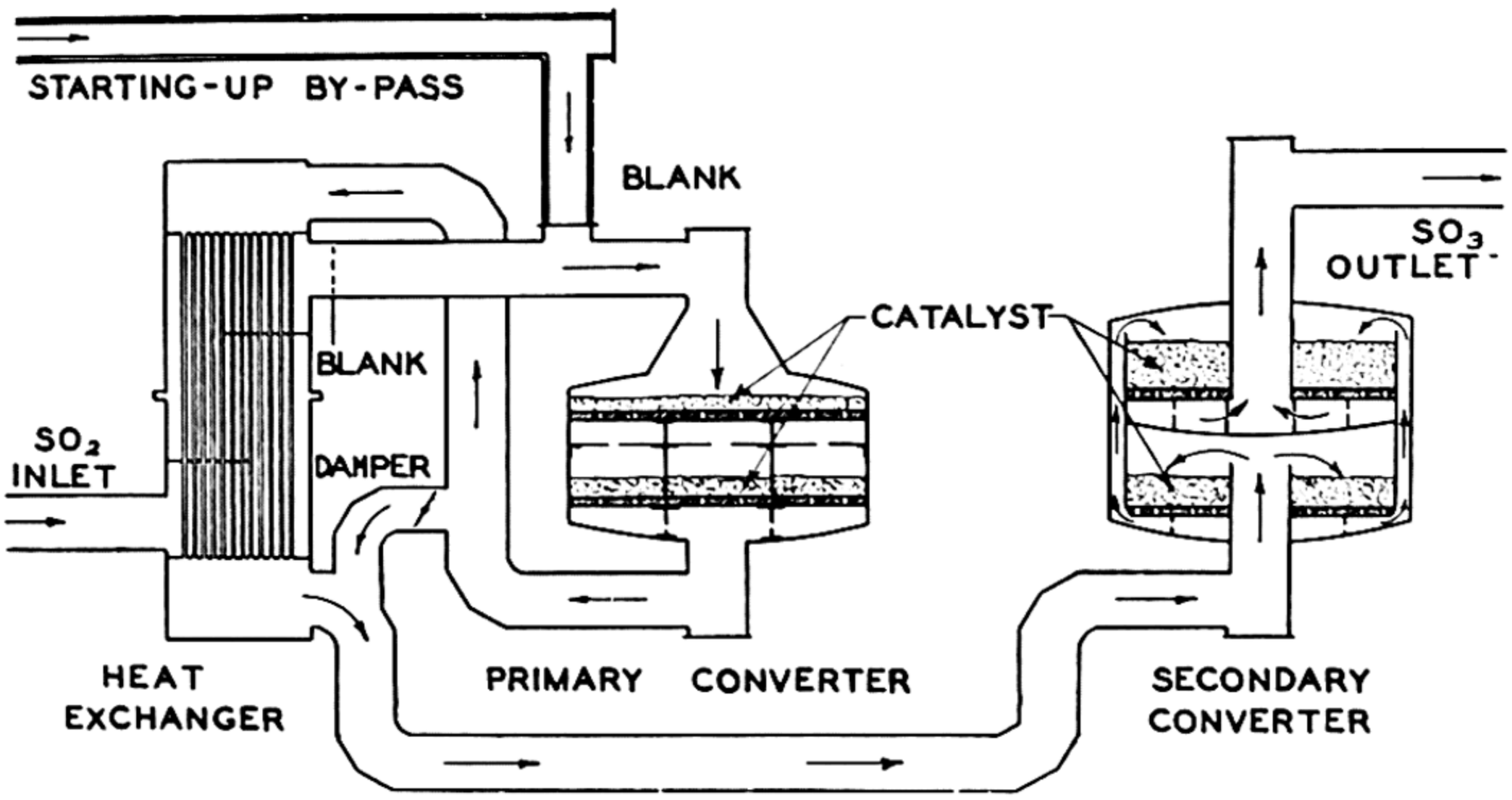


FIGURE 13.—Tray-type converter assembly-flow diagram, for the conversion of sulfur dioxide to sulfur trioxide. (Drawn from sketch kindly furnished by Chemical Construction Corp., New York.)

Control of Operation. The plant is practically automatic. No labor is required except for charging the sulfur. The operation of the sulfur burner is controlled by the temperature of its exit gas, which affects a resistance pyrometer; should the temperature drop, a Wheatstone bridge is unbalanced, and the current which can flow actuates a control which in turn allows more steam in the turbine, so that more sulfur is delivered to the burner. The volume of air is set. If the temperature of the exit gas rises, the opposite action results in decreasing the steam on the turbine.

The 98 per cent acid is controlled by measuring its electrical conductivity, and this is checked periodically by the "heat rise" test, as follows: 200 cc. of 105 per cent H_2SO_4 at temperature T_1, and 200 cc. of the acid to be tested having temperature T_2, are poured together and the temperature of the mixture, T_3, noted. The value of R is found from the expression

$$R = T_3 - \frac{(T_1 + T_2)}{2}$$

Table 3 gives the percentage of the acid tested.

[5] General Chemical Division, Allied Chemical and Dye Corporation, New York.

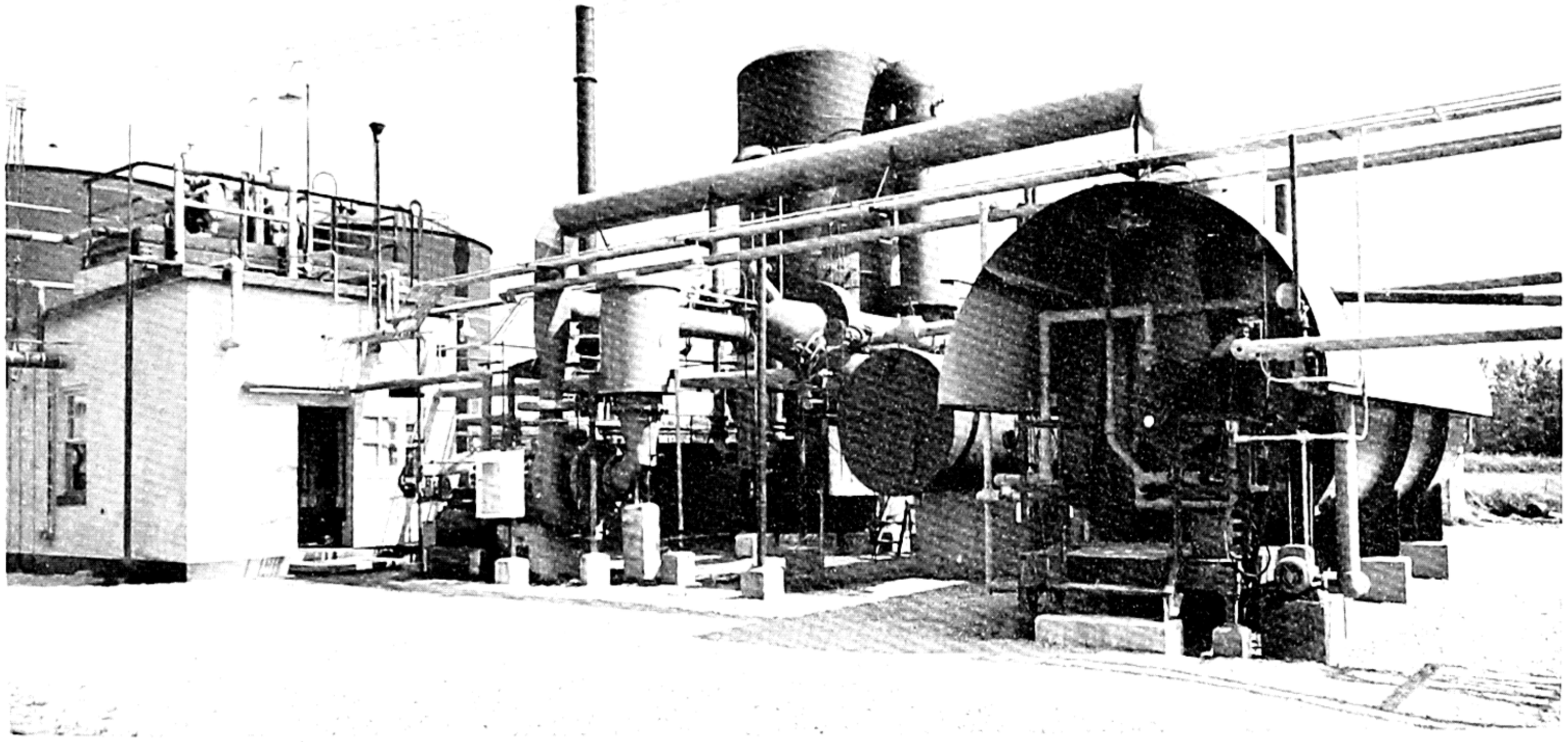


FIGURE 14.—The American Cyanamid Company's new sulfuric acid plant at Hamilton, Ohio. It is the New Type Chemico Contact Plant, of 50 tons per day capacity. Visible from right to left, the sulfur spray type combustion furnace, waste heat boiler, air filter, turbo blower feeding air to the furnace, control house, and acid storage tanks. The tall structure in the background is the quench converter (in which the gases are cooled by the direct admission of cold air, a new development), with the pipe carrying the gas from the furnace entering near the top. One end of the absorber is just visible behind the Converter. The exit gas plume [on exit stack from P-A Venturi scrubber] is essentially steam, with no acid mist. (Courtesy Chemical Construction Corporation, New York).

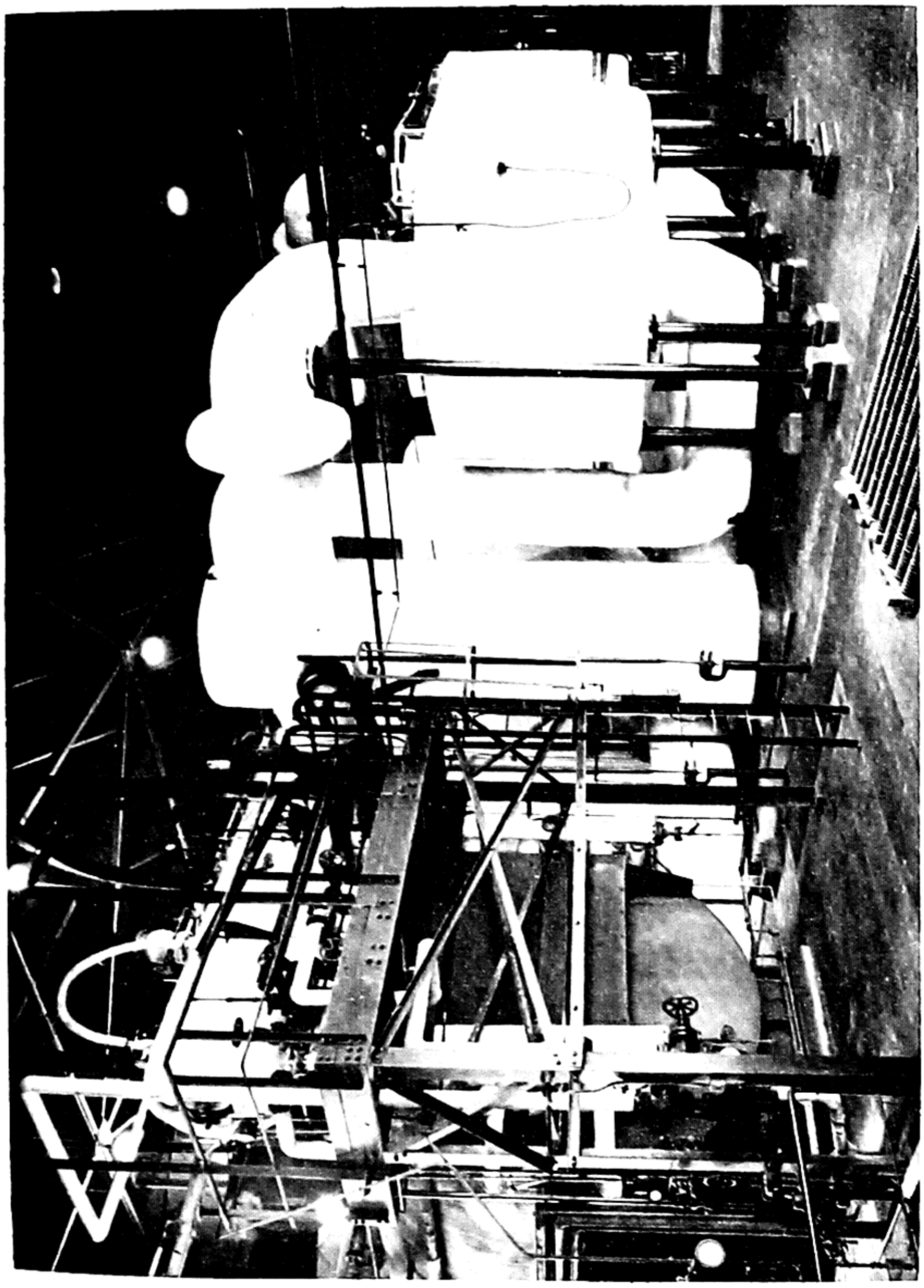


FIGURE 14a.—A view in a sulfuric acid contact plant of the standard type, with tray style converters. The two converters (the taller vessels at right) and heat exchangers (the two lower vessels to the left) are heavily insulated. (Courtesy of the Chemical Construction Corporation, New York).

The strength of the 20 per cent oleum and of the 93 per cent acid is tested by a hydrometer.

The pressure of the air when let into the burner is 55 inches of water; of the gas entering the converter, 43 inches; leaving the converter, 15 inches; hence there is a differential of 28 inches due to the converter mass. Should this differential increase to a certain higher figure, it would mean that the mass was dirty, or had become plugged in some other way. It is then time to clean the mass, or to replace it.

TABLE 3.—*Testing of 98 per cent acid for strength by the heat rise test.*

R	Per Cent H_2SO_4	*R*	Per Cent H_2SO_4
2° C.	99.9	18° C.	97.5
4	99.5	20	97.3
6	99.3	22	96.9
8	99.0	24	96.4
10	98.7	26	96.2
12	98.4	28	96.1
14	98.1	30	95.8
16	97.8		

In a number of plants, it has become the practice to filter the molten sulfur, in order to remove suspended fine solids (mineral ash, fly ash) and feed only clean sulfur to the acid train. Certain operators find it advisable to filter the hot sulfur gas from brimstone about to enter the converters by means of graded silica chips, for example. The catalyst itself may contribute dust which tends to clog the converter, by the rubbing of pellets against each other. By shutting down the unit and screening the pellets, the mass may be restored to normal service.

Other Processes. An installation using brimstone sulfur with the Monsanto vanadium catalyst has a compactness[6] similar to that of the Chemico process and an operation similarly neat. The Monsanto system has the two-pass converter system, that is, two converters with an inter-cooler between them is preferred. The first converter carries substantially 30 per cent of the catalyst and gives from 75 to 80 per cent of the conversion; the gas leaving this converter has a temperature of about 580° C. (1076° F.). It is cooled to 400° C. (752° F.) in the inter-cooler and enters the second converter at that temperature. In this one, the heat rise is moderate, 45 to 60° C. (81 to 108° F.), so that complete conversion of the small amount of SO_2 entering it is assured. Conversions of 97 and 97.5 are reported.

In an English plant recently described,[7] the sulfur burner is a brick-lined upright cylinder, with an arch one-third of the way down which has a central opening. The arch supports a checker-work of firebrick set in the form of a pyramid. Molten sulfur from the melter (steam coils) purified by passing through a screen and by settling in a cone, is pumped by a positive rotary pump into the top of the burner, where the dried and heated combustion air also enters; the two travel concurrently downward. The re-

[6] Daniel S. Dinsmore, *Trans. Am. Inst. Chem. Eng.*, 26, 158 (1931). The catalyst mass resembles split peas.

[7] *The Industrial Chemist (London)*, 22, 525 (1946).

sulting 7 per cent sulfur dioxide gas, at a temperature of 940° C. (1724° F.) is cooled to 420° C. (788° F.) in a waste heat boiler, is filtered free from dust in a hot gas filter, and is ready to enter the first converter. The combustion air is dried in a drying tower, as in the Chemico plant described, and is heated by interchange with the sulfur trioxide gas leaving the second converter. The first converter contains about one-third of the total catalyst, and an 80 per cent conversion takes place. The gas leaves at 550 °C. 1022° F.), is cooled in a heat exchanger against air, which in turn preheats the boiler feed water, and then enters the second converter, where a total conversion of about 97.5 per cent is reached.

The Badische process, which uses platinized asbestos, installed in many American plants in the period preceding the war of 1914-18, operated with converters and transferrers separate, with a by-pass to regulate the temperature of the gas.[8] Most of them continue in service.

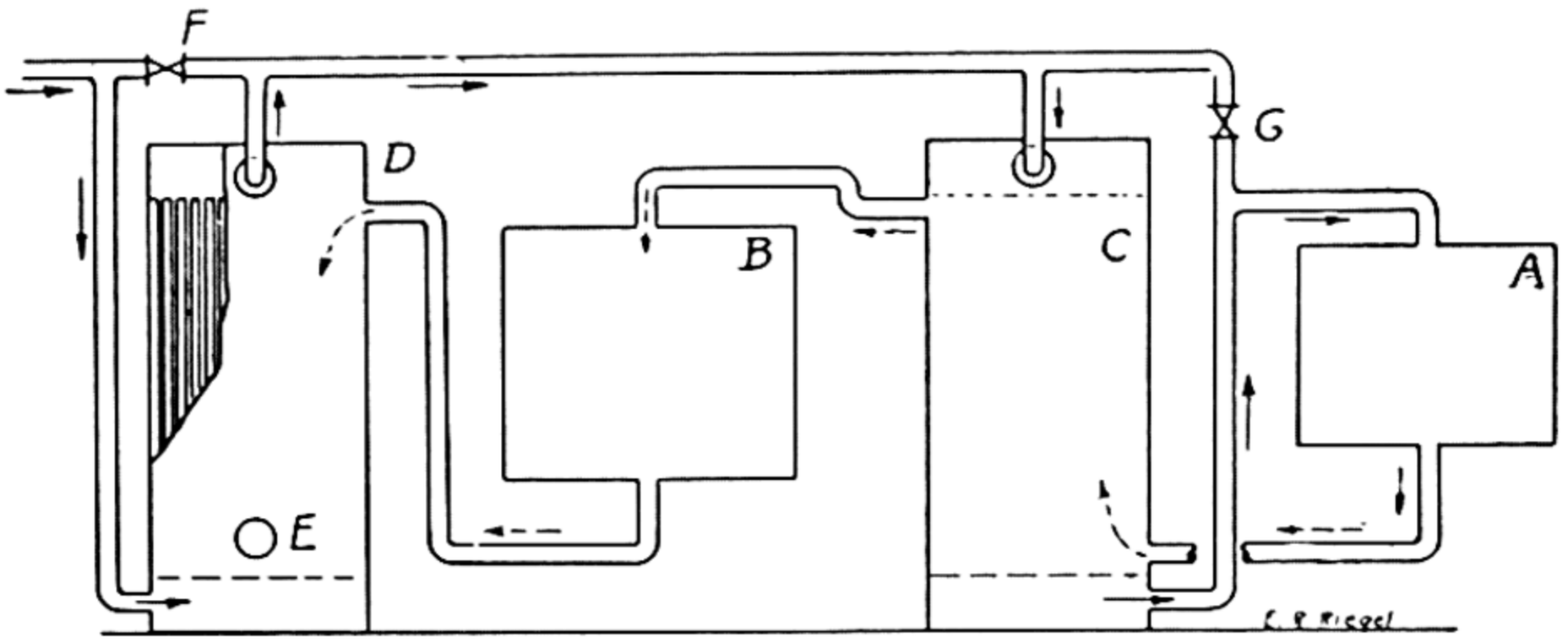


FIGURE 15.—Circulation of gases through converters and heat transferrer in the Badische system. A, first or short converter; B, second converter; C and D, heat transferrers; E, outlet for the SO_3 gas to absorbers and coolers; F and G, by-pass valves through which a certain amount of cold gas may be constantly admitted. The direction of the gas is shown by arrows. The sulfur gas enters at upper left.

The Grillo-Schroeder system, installed in numerous American plants, which uses a calcined magnesium sulfate as platinum carrier, also continues to give excellent service.

The tendency is to change over to vanadium oxide when the opportunity offers itself.

Other systems among the older ones that should be mentioned are the Tentelew[9] system (platinum) and the Mannheim system (iron oxide).

A remarkable process is the one reported from Trail, where, during the war years at least, a contact installation with vanadium catalyst was served with a sulfur gas of high SO_2 content and high oxygen content, with excellent result.[9a] The gas entering the converter contained 25 per cent SO_2,

[8] Described in some detail in the first edition of this book, where the purification of sulfur gas from Herreshoff and similar burners using pyrite is considered. Flow sheets for the Badische, Grillo-Schroeder and Mannheim systems will be found on page 150, Bureau of Mines Bulletin 184.

[9] See German Patent 227,095 which has a sketch showing the radiating pyramids peculiar to this system.

[9a] "A cyclic process of sulfuric acid manufacture at Trail, B. C.," A. F. Snowball, *Can. Chem. and Proc. Ind.*, 32, 1110 (1947).

30 per cent oxygen, and 45 per cent nitrogen. A source of 100 per cent SO_2 available for the production of elemental sulfur in a separate operation could be tapped, and a 99 per cent oxygen was available as by-product from electrolytic hydrogen cells. The gas leaving the converter was cooled, its sulfur trioxide removed by solution in acid, and the residual gas recycled, after addition of the required make-up gases. Accumulation of nitrogen beyond the 45 per cent figure is prevented by a constant purging. The catalyst on the topmost of the two trays in the converters was the standard pellet size, 0.55 centimeter diameter by 0.59 centimeter long; on the second tray, a larger size for experimental purposes. The plant adapted to this process was an obsolete standard contact plant, rated at 35 ton daily capacity. Fed with the rich gas and otherwise modified, it produced finally 200 tons of 100 per cent sulfuric acid per day.

The Various Catalyst Masses. The catalyst masses of modern type best known in the United States are listed in Table 4, with their density, efficiency,

TABLE 4.—*SO_2 to SO_3 catalyst masses.*

	Apparent density of mass	Daily pounds of sulfur as 8 per cent SO_2 gas converted per liter of catalyst mass	Appearance
Selden mass, V_2O_5	0.46	5	Light greenish-yellow tablets ¼" diameter
Monsanto mass, V_2O_5	0.56	5	Light green half-cylinders ⅜" length

For these two masses, a volume of catalyst fluctuating between 125 and 175 liters will be required for the production of one ton of 100 per cent H_2SO_4 per day.

and appearance. The efficiency is in terms of the daily pounds of sulfur as 8 per cent SO_2 converted per liter of catalyst mass.

A sample of spent vanadium catalyst from another source consisted of pellets which were light green with brown areas. The pellets contained about 5.5 per cent V_2O_5. The catalyst was probably prepared by soaking aluminum oxide (or silica) pellets in a solution of ammonium metavanadate, then drying and calcining them; a film of oxide is thus formed on the surface of the catalyst.

The life of all catalysts is variously given as several years.

Preparation of the Selden Mass. The vanadium pentoxide mass known as the Selden mass, developed by Dr. Jaeger, and used for the Chemico installation just discussed, is made as follows:[10]

"A." A solution of potassium silicate is sprinkled on diatomaceous earth; and the wetted particles are mixed by shoveling and raking.

"B." Potassium aluminate is made from potassium hydroxide and alumina, in the form of a solution.

[10] Taken from the court findings, Federal District Court for the Western District of Pennsylvania, in the case of the General Chemical Co. vs. the Selden Co.; the former claimed infringement of its patent 1,371,004 (Slama and Wolf). The court decided that the Selden Co. was not infringing (June 17, 1932), but the case was reopened and evidence taken before a special Master; in 1938, the controversy was finally settled in favor of the Selden Company.

Two equivalents of "B" are sprinkled on 5 equivalents of "A," and well mixed. The potassium aluminate and potassium silicate form a zeolite, of jelly-like consistency.

"C." Ammonium vanadate solution (3 equivalents) is added to potassium aluminate (1 equivalent) and potassium hydroxide, forming a thick gelatinous suspension which can just be poured; it contains a complex vanadium compound.

"C" is poured onto the soft zeolite-coated diatomaceous earth, mixed only slightly, without penetration. The lumps which form are compacted, screened, a small amount of stearic acid added (as lubricant) and formed into pellets ¼ inch in diameter. The pellets are calcined or sulfated by heating in a current of 1 per cent SO_2, gradually raising the heat to 500° C. (932° F.) and increasing the proportion of sulfur dioxide. After calcination, the pellets are cooled in a current of air, and are packed in air-tight containers, for shipment. This is the finished catalyst, ready for the converter.

During the calcination, vanadium pentoxide is formed, but it remains in intimate contact with the other constituents of the pellets.

Badische Mass. A vanadium mass successfully used by the Badische Aniline and Soda Fabrik, in Germany, is made as follows: 316 parts of kieselguhr are mixed with a solution of 50 parts of ammonium vanadate and 56 parts of potassium hydroxide; enough water is evaporated to allow the formation of granules. These are heated at 480° C. (896° F.) in 8 per cent SO_2 gas, then cooled in a current of air.

The original Badische mass, platinized asbestos, is made by dipping fibrous asbestos into a solution of ammonium chloroplatinate, working the asbestos around until every fiber is coated. The yellow mass is then placed in the converter, and calcined with a lean sulfur gas. A gray mass results which resists the high temperature of conversion.

Poisoning. The bugbear of the early contact operators was the "poisoning" of the platinum mass. There are two kinds of poisoning: temporary poisoning due to chlorine, which relieves itself as halogen-free gas sweeps through the converters; and permanent poisoning, due to arsenic. In the early days of the contact process, operators were surprised that burner gas from pyrite ore, fed to the new system, gave rise to difficulties, while in the chambers they functioned smoothly; the equipment for purification from chlorine and arsenic was soon evolved, and poisoning became a matter of faulty operation. Arsenic as arsine, AsH_3, was avoided by not using iron for the coolers, so that condensed acid could no longer react with iron and form the hydrogen necessary for the formation of the gas. Lead is used instead.

Purification of Gas from Pyrite Ore

Although at the present time (1947) some 75 per cent of the total sulfuric acid is made from sulfur, there are still important installations in which iron pyrite, and especially pyrite fines, is the source of the sulfur gas. The purification of such gas must be performed with greater care and carried further, in order to use the gas in any contact system. How long the lavish use of elemental sulfur can continue is a serious consideration, for the resources of mineral sulfur are distinctly limited.[11]

The gas from a Herreshoff rotary shelf burner for fines (page 12) or from

[11] "Economic position of sulfur," A. M. Taylor, *Ind. Eng. Chem.*, 24, 1116 (1932).

flash combustion is cleared of its iron oxide cloud in dust chambers, or dust collectors, with or without a "hot Cottrell" precipitator following, all working on the hot gas. The gas next passes through short lead towers, meeting a flow of sulfuric acid, which cools the gas somewhat and removes the arsenic in the form of oxide; this tower, it may be noted, imitates the Glover tower. After this, the gas is cooled to room temperature in water-cooled 8-inch lead pipes; it then enters coke-packed lead boxes, a wet box followed by a dry one, to remove chlorine, present in the form of hydrogen chloride, and to arrest the acid mist; the clean gas then enters the blower which feeds it to a drying tower with 62° to 66° Bé. (81.3 to 93.2 per cent) sulfuric acid as the drying medium. (*See* Figure 16.) The gas is now ready for the converters;

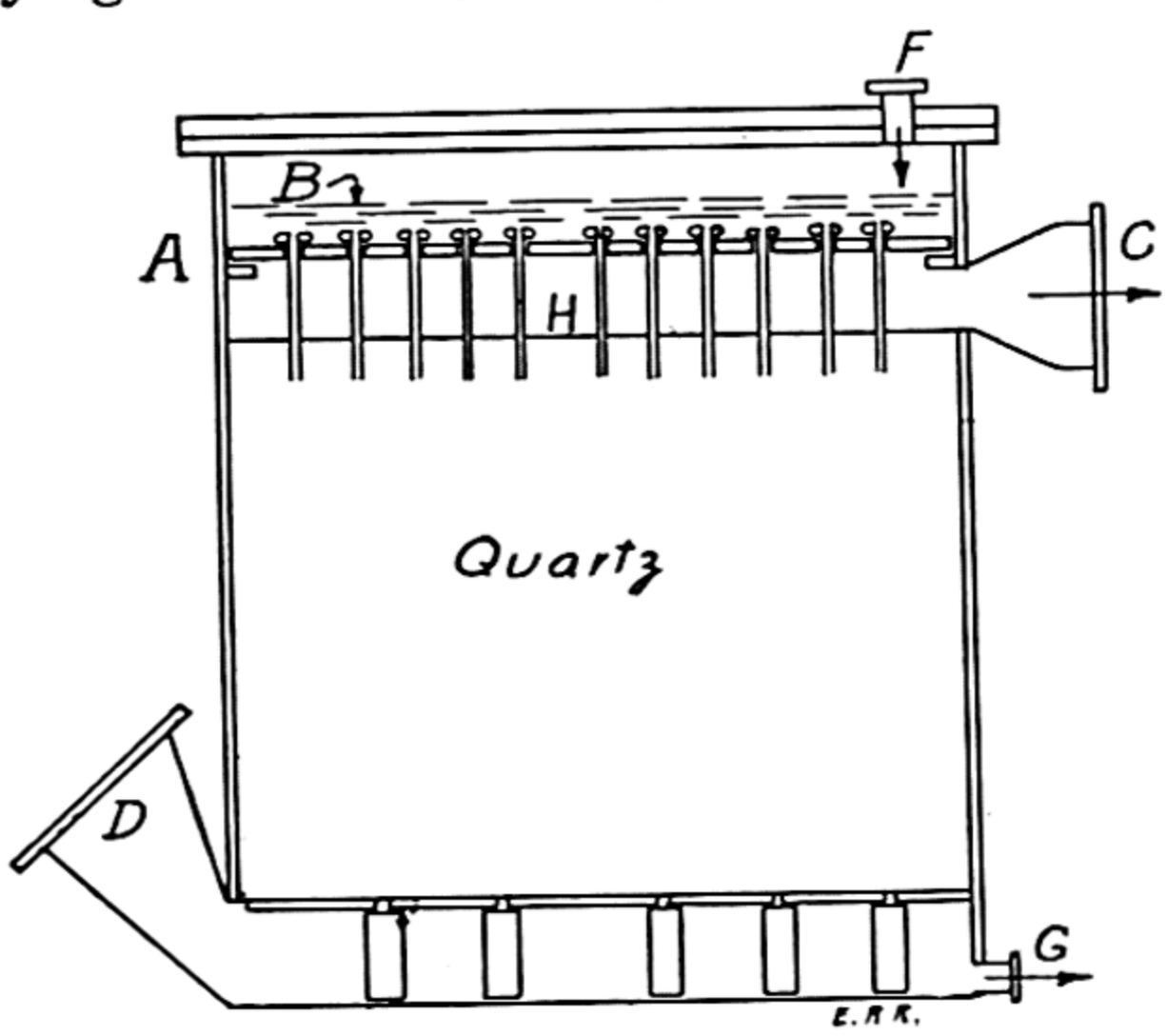


FIGURE 16.—The drying tower; *A*, circular plate bearing the porcelain tubes; *B*, level of the acid in the acid chamber; *C*, outlet for gas; *D*, inlet for the gas; *F*, inlet for the acid; *G*, outlet for the acid; *H*, upper level of the quartz packing.

it may be preheated within the converter, as was done in the early Chemico construction, or by outside multi-tubular heat exchangers.

Alternate arrangements provide for water-washing in a tower just beyond the "hot" or "dust" Cottrell, and this tower is followed by a second Cottrell, called the "moisture" Cottrell.

The melting points for sulfuric acid of various strengths and for the oleums are extremely irregular; they are shown in Figure 17 by means of a graph. The specific gravity of the acids increases gradually to 1.8415 for the 97.70 per cent H_2SO_4, which is the maximum; it then decreases slightly to the 100 per cent acid. As a result, the specific gravity as a measure of strength over that range (96 to 100 per cent) might lead to gross errors; for that reason, conductivities are used instead.

The oleums also have a maximum specific gravity, more pronounced at 45° C. (113° F.) than at 15° C. (59° F.), as indicated in the figure.

YIELDS

A conversion of 97 per cent of sulfur dioxide to the trioxide is good practice. The unconverted gas is lost to the atmosphere on issuing from the last absorber. When sulfur as brimstone is the starting material, additional losses are only those due to the impurities in the brimstone, which remain in the

melting tank, and generally are below 1 per cent of the weight of brimstone. The over-all yield may be about 95 or 96 per cent.

When iron pyrite is used as fines, there is a loss of about 2 per cent sulfur to the cinders. Losses occur in the scrubbing towers, coke boxes, electrical precipitators, and to a slight extent in the drying tower, so that an over-all yield of 90 to 92 per cent would be fair.

The cost of raw materials has been mentioned previously. The selling price for oleums is higher than for 66° Bé. acid, which in turn is higher than for the weaker acids; the price is roughly proportional to the sulfur trioxide content. The price for chamber acid (50° Bé.) depends upon many factors,

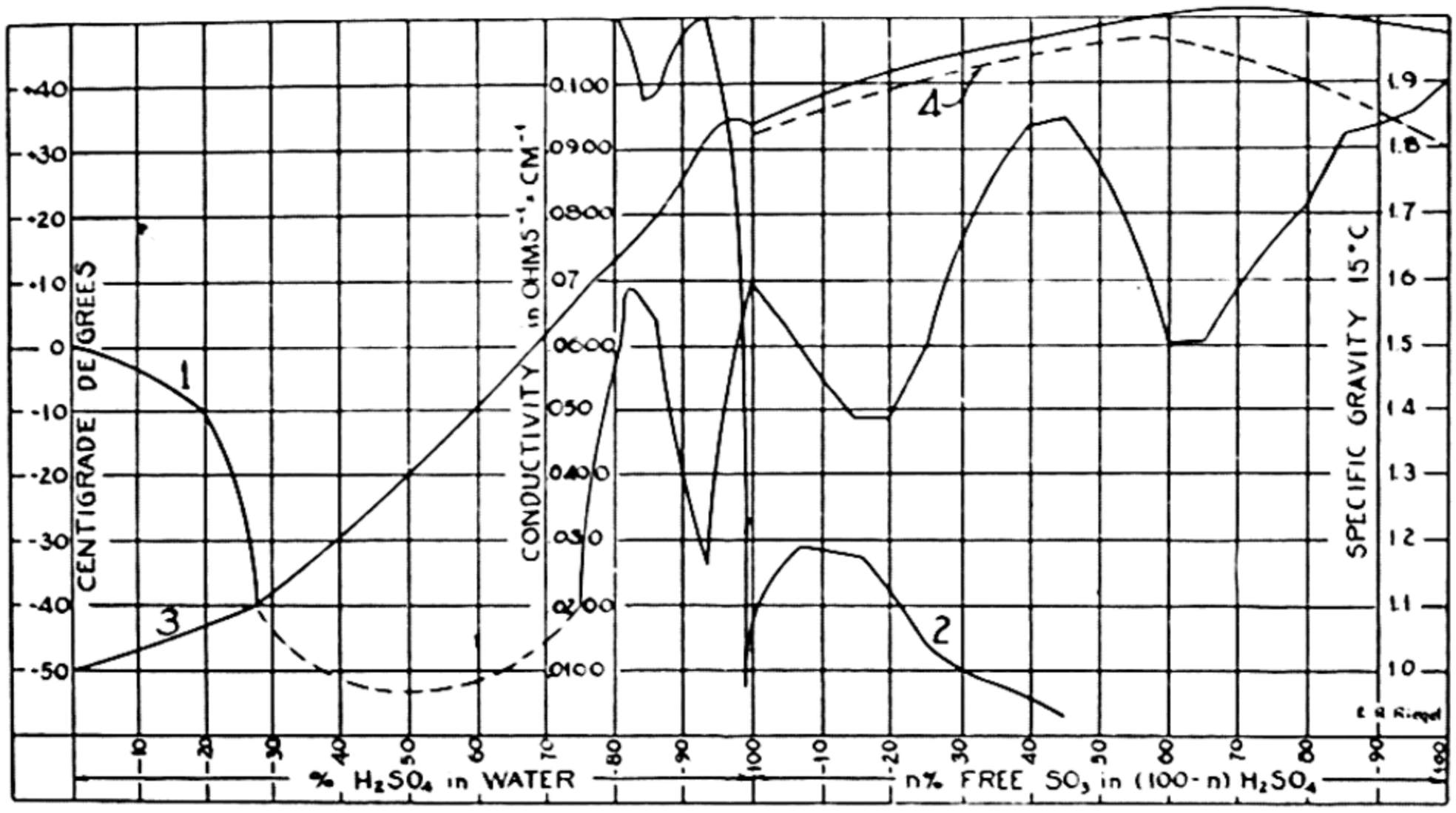


FIGURE 17.—Physical properties of sulfuric acids and oleums of various concentrations. 1, melting points (Knietsch); 2, conductivities in reciprocal ohms (Landolt-Börnstein Tabellen); 3, specific gravities at 15° C.; 4, at 45° C. (Knietsch).

and this acid moves mainly within fertilizer factories; it has been as low as $7.75 a ton. The price to the customer for 60° Bé. acid is $12.50 a ton; 66° Bé., $15.50; 20 per cent free SO_3 oleum, $18.00; while the price for 65 per cent free SO_3 oleum, the strength most generally favored, is $42.00 a ton, all for tank-car lots (May, 1948). The new 100 per cent SO_3 grade ("Sulfan") is available at this time in drum lots only, at $55.00 a ton; the price will be lower in tank-car lots.

Acids of 66° Bé. and higher strengths are stored and shipped in steel tanks, weaker acids generally in lead-lined tanks. Smaller lots are shipped in glass carboys. Acid from 61° to 65° Bé. may be shipped in steel tanks if the acid contains an inhibitor (against corrosion).[12]

Concentration of Diluted Sulfuric Acid. In many operations, the sulfuric acid functions as a water-remover; in others, it may remove water and

[12] Regulation of the Bureau of Explosives, Interstate Commerce Commission. Inhibitors are organic substances, such as sulfonated slaughter house waste, used in small quantities. "Practical application of inhibitors in pickling operations," F. N. Speller and E. L. Chappell, *Chem. Met. Eng.*, 34, 421 (1927). See also "reading references." The statement is made that 59 or even 58° Bé. acid is regularly shipped in steel tank cars without any inhibitor.

have another function besides. The water taken up by the acid dilutes it, and it is essential that it be removed, so that the acid, restored to its former higher strength may be used over again. In nitrations, in which mixed acid is generally used, there results a spent acid containing very little nitric acid, and with its sulfuric acid diluted. The concentration of spent acid becomes a major process when large quantities are required, because transportation by freight, and the time required for such transportation, must be reduced.

In the Kalbperry concentrating tower the rising, hot combustion gases from an oil or other burner come in contact with the descending acid; water

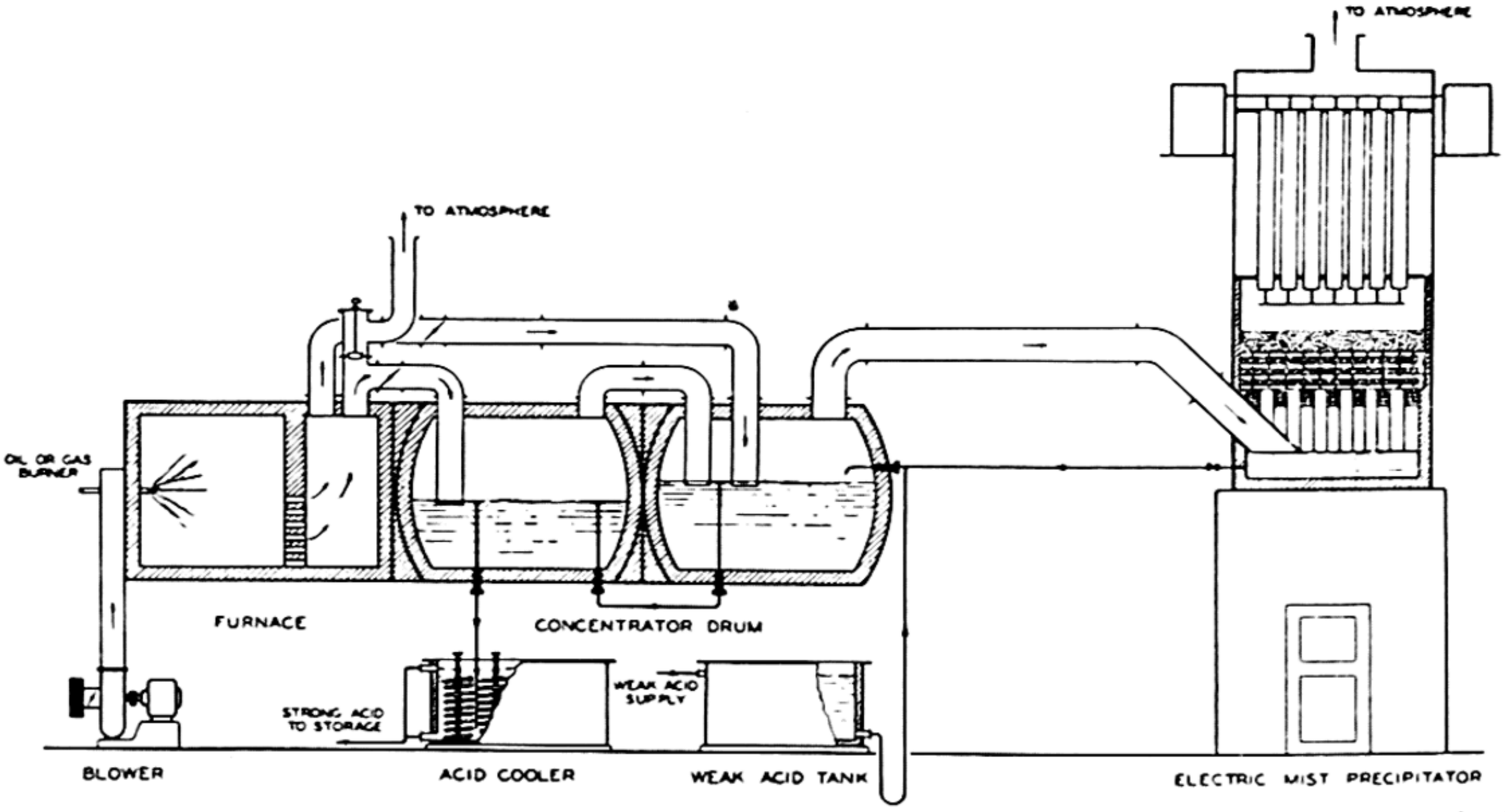


FIGURE 18.—Drawing of a diagrammatic cross section of the latest design "Chemico" drum type sulfuric acid concentrator. Note the cooling coils for the strong acid leaving the first compartment (see text). (By courtesy of the Chemical Construction Corporation, New York.)

is driven out while strong acid collects at the base of the tower. The gases leaving the tower pass through a coke box or a Cottrell precipitator in order to deposit the mist. In America, the tower has been successfully used for the production of 96.5 to 97 per cent sulfuric acid from spent acid containing 68 to 70 per cent,[13] while in England, Parrish, a well known engineer, prefers to concentrate only to 90 to 92 per cent by any device which brings hot gases and the acid in contact,[14] and prefers a pot still, or a special vertical-tube concentrator with especially wide tubes for higher strengths. The Chemico drum type concentrator (Figure 18) has been used with success in the United States as well as in other countries. The entire unit is constructed in the shape of a single cylindrical tank, with the exception of the electrical precipitator which removes the mist from the final gas. The acid compartments are lined with lead and acid-proof masonry, and the furnace end with

[13] Page 138, "The manufacture of sulphuric acid in the United States," by A. E. Wells and D. E. Fogg, Bureau of Mines. Bulletin 184 (1920) where a plan and elevation of the complete concentrator is shown.

[14] "Concentration of sulphuric acid, modern plant development," by P. Parrish, *The Industrial Chemist (London)*, 17, 41 (1941).

fire and insulating brick. The combustion gases from the burner travel through iron and acid-proof iron pipes. The acid is concentrated in two stages; the highest strength is the acid in the compartment nearest the furnace, which receives the hottest gas. All the gas and vapors leaving the first compartment enter the second compartment, where they contribute to the evaporation, yet lose instead of gain in sulfur trioxide content. The gases escaping through the stack of the electrical precipitator are fire gases and water vapor; acid which collects at its base is fed to the second acid compartment. The electrical precipitator may be omitted. Due to the blast of air and fire gases, the concentrating temperature is about 100° F. (37.78° C.) below the corresponding boiling point recorded in the tables

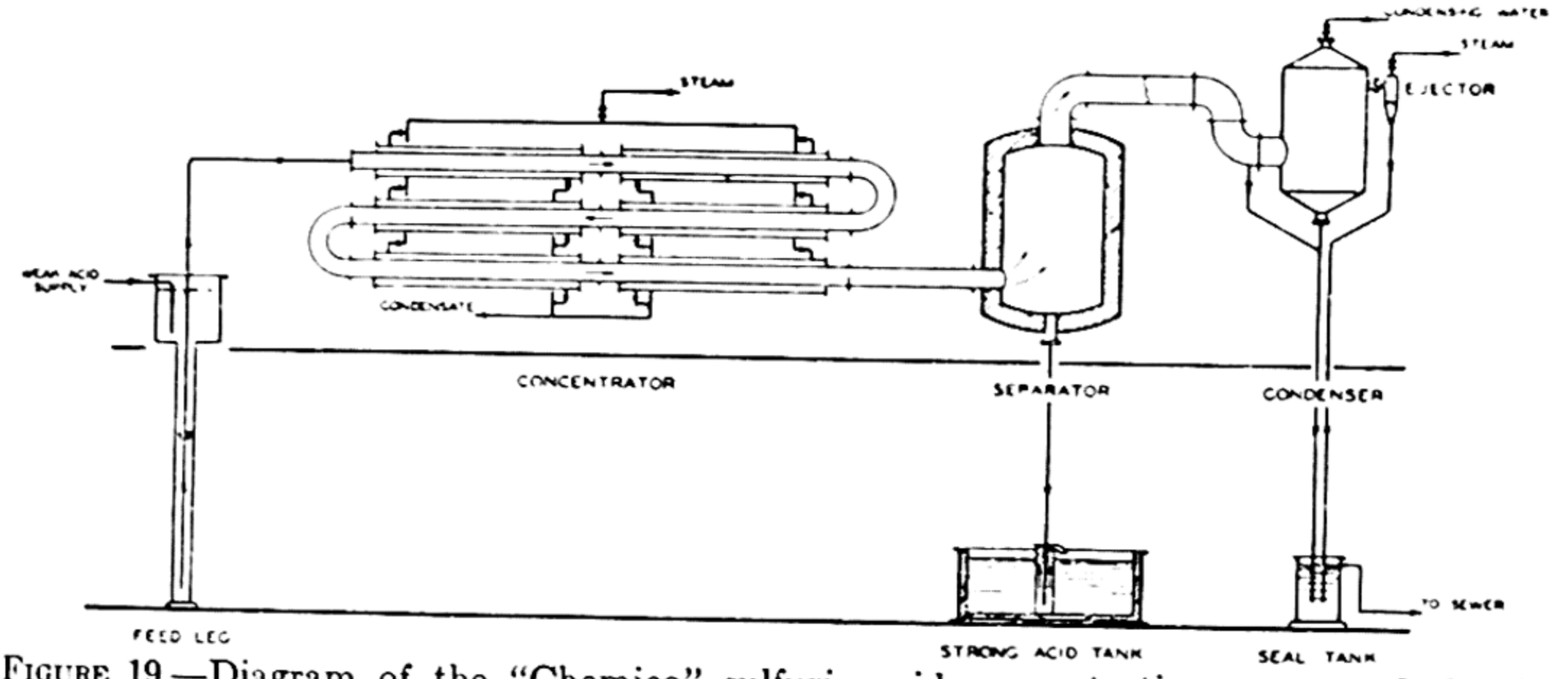


FIGURE 19.—Diagram of the "Chemico" sulfuric acid concentrating process, flash film vacuum type. (Courtesy of the Chemical Construction Corporation, New York.)

for the particular strengths. The result is high heat efficiency. Some of the hot gases from the burner may be by-passed to the second or low-stage drum compartment, so that the evaporative work done therein may be regulated. The depth of the seal at the various gas inlet pipes is very slight, so that the back pressure is slight and power is a minimum.

The Chemico Flash-Film Vacuum-type Concentrator works under a vacuum induced by a steam jet condenser and barometric leg. The acid, lifted from the feed leg by the vacuum, cascades from one pipe to the next, over half-moon dams just indicated by a vertical line in Figure 19. The concentrating pipes are acid-proof iron, steam-jacketed, with concentric steel pipes and packing glands. The amount of feed acid entering in measured quantity is balanced against the heat input and vacuum to regulate the strength of the finished acid and the output from the unit. The flash-film concentrator is the proper choice where steam is cheap and water is plentiful.

Other processes are the cascade system, using quartz, Duriron, or other acid-proof metals; the Gaillard and the Kessler, both used mainly in Europe; the du Pont falling film concentrator,[15] the Simonson-Mantius concentrator,[15] and others.

[15] For both of these, see "Sulphuric acid concentration, a summary," *Chem. Industries*, 60, 50 (1947).

Recovery of Acid from Waste Products. There are processes which leave a sulfuric acid not only diluted, but charged with impurities, such as tarry matter from the treatment of petroleum fractions. Some of these sludge acids are so difficult to separate into acid and sludge that it has been found advantageous to make sulfur dioxide out of residual acid (with or without auxiliary sources of sulfur dioxide), and remanufacture sulfuric acid from it in a vanadium type converter. There is produced clean and strong sulfuric acid, and a second product, a granular fuel. This is the Chemico sludge conversion process[16] devised by the late Dr. H. Hechenbleikner.

The sulfuric acid in copperas may now be recovered by roasting the copperas with pyrite in rotary furnaces, or by heating the previously dehydrated copperas with coal, under definite conditions.

The Rôle of Sulfuric Acid

The uses of sulfuric acid are as varied as chemical technology; it is among the acids what lime is among the alkaline agents. If it is required merely to provide an acid state, sulfuric acid is chosen, provided it is not unsuitable for special reasons. Many of its numerous applications are given in subsequent chapters. A table of its distribution follows.

Table 5.—*Distribution of sulfuric acid, as reflected by the allocations of sulfuric acid in the war program.**

Direct military uses		14.1%
Export		0.1
Other uses:		
Chemical manufacture		24.4
Ammonium sulfate	4.0%	
Aluminum sulfate	2.4	
Hydrochloric acid	1.5	
Hydrofluoric acid	1.3	
Sodium phosphate	0.7	
Primary chromium chemicals	0.4	
Phenol	0.3	
Other chemicals	13.8	
Superphosphate		17.8%
Petroleum refining		15.9
Metallurgy		7.0%
Iron and steel	5.8%	
Other metallurgical	1.2	
Lead, zinc and titanium pigments		5.8%
Rayon		3.5
Rubber		0.7
Industrial explosives		0.6
Silica gel		0.5
Miscellaneous uses		9.7

Based on the six months period, January 1 to June 31, 1945. The total allocations were 7,134,285 short tons of 100 per cent acid, and included unspecified tonnage of fortified spent acid.

* "Facts for Industry," Bureau of the Census.

[16] "Production of contact sulfuric acid from refinery acid sludge," by S. F. Spangler, Proc. 14th annual meeting Amer. Petroleum Institute, October 26, 1933, with a diagrammatic lay-out; or "Sulfuric acid from refinery sludge," an illustrated flow sheet, *Chem. Met. Eng.*, 48, 144 (1941).

The production of sulfuric acid has been stimulated by war demands. In 1941 the production, 10,944,000 tons of 50° Bé., was an increase of 19 per cent over 1940, itself larger by 11.3 per cent than the production in 1939. In 1945, the production, 9,522,136 tons expressed as 100 per cent sulfuric acid, was 47 per cent larger than the 1941 production. (Later figures in Part I.)

The weak acid from the chambers has remained important because a dilute acid is required in the manufacture of superphosphate of calcium, a fertilizer. The standard chamber plant has the advantage of having no license fees to pay; the newer processes of necessity involve such payments which the acid produced must carry.

For many purposes, such as nitrations and sulfonations of organic substances, a strong acid is required, such as 98 per cent H_2SO_4 or an oleum; the contact process must furnish these. Furthermore, an oleum may be used to bring a weak spent acid to the reaction strength,[17] so that here also, the product from the contact plants offers an advantage; it may be said in fact that contact acid will do everything that chamber acid does; but the converse is not true. Finally, contact acid is very pure, and is selected for certain uses for that reason.

Sulfuric acid is no longer indispensable for making nitric acid of low strengths, such as 61 per cent HNO_3, now that the catalytic oxidation of ammonia has been perfected. To make concentrated acid from such low-strength nitric acid, sulfuric acid remains necessary.

Sulfuric acid occupies its important position because the raw materials are cheap, the methods of manufacture are highly developed, and no fuel is required, except for a small amount of power. When close to smelters, the raw material for producing the sulfur dioxide may be said to cost nothing at all. The degree of perfection reached in both chamber and contact processes is remarkably high. The plants are practically automatic. Hand labor is needed to charge the sulfur to the melting tank; for the burners for fines, an operator must bring the ore to the top of the burners, by means of an electric truck. From that point on, the process runs by itself. As to supervision, one chamber man can watch and regulate one or more sets; in the contact process, one operator takes care of several units, by reading pressure gages, thermometers and thermocouples, by making chemical or thermal analyses on the sulfur dioxide gas and exit gas, and by hydrometer and conductivity readings. Some of these means of control are automatic or automatically recording, simplifying the supervision still further. A small force of laborers is required for clean-out gangs, and skilled labor for repair gangs. Labor-saving devices and automatic continuous operation distinguish the sulfuric acid industry even in an age which is characterized by them.

Other Patents

U. S. Patents: 1,660,511, on the automatic heat exchange converter for contact process; 1,675,308, on the micro-porosity of vanadium mass structure, with 23 examples

[17] This is of limited applicability, for a balance must be maintained; a volume of acid greater than can be used must be avoided. With 100 per cent oleum, this difficulty disappears.

of preparation formulas; 1,675,309, vanadium pentoxide masses on quartz as carrier, with several examples; 1,694,123, also on vanadium pentoxide masses with porous structures; 1,657,754, on vanadates and tungstate for the catalyst mass, with 20 examples; 1,657,753 and -4, 1,695,285, 1,696,546, 1,701,075, all on vanadium masses; 1,741,310, on stabilizers in vanadium masses; 1,518,043, on vanadium mass to be preceded by some platinum; 1,450,661, on construction of converter, as also 1,685,672, 1,660,511, 1,857,308; 1,862,746, on drying tower construction and operation (*see also* 1,384,566, 1,824,896); 1,912,832, manufacture of sulfuric acid by means of nitrogen compounds, to Andrew M. Fairlie; 1,995,292, manufacture of sulfuric acid; 2,028,739, sulfur dioxide from Spanish pyrite, removing fluorine by silica, and otherwise purifying the gas; 2,008,761 and 1,970,923, process and apparatus for producing sulfur trioxide; 2,042,675, making sulfuric acid from a sulfur dioxide containing organic impurities; 1,995,360, 2,023,203, 2,028,416, making sulfuric acid or sulfur dioxide; 2,001,359, making concentrated sulfuric acid or oleum from sulfur dioxide regenerated from sludge in petroleum refineries, to the late Ingenuin Hechenbleikner; 1,996,764, production and purification of sulfur dioxide from similar spent acid; 2,044,960, production of sulfur dioxide and iron oxide; 2,030,885, apparatus for burning sulfur; 1,942,817, catalytic apparatus; 1,971,465, catalyst for use in the contact method of making sulfuric acid, containing thallium and vanadium; 2,030,021, method and apparatus for the production of sulfur dioxide, by roasting ore; 2,198,795, on tray type sulfuric acid converter; 2,172,617, for making high strength H_2SO_4; 2,258,938, on a nitric oxide-sulfuric acid process; 2,255,445, sulfuric acid and iron oxide from waste pickling acid. U. S. Pat. 2,406,890 on recovering spent sulfuric acid from alkylation sludge; U. S. Pat. 2,406,930 to Nicolay Titlestad, on recovering sulfuric acid values from spent acid from nitrations.

German Patents: 459,978, sulfuric acid made in towers by an excess of nitrous gases; 463,828, on chamber acid; 455,075, for atomizing sulfuric acid; 467,587, on making all the acid in the Glover tower; 466,578, making oleum by contact process; 516,764, on a catalytic mass containing chromium hydroxide; 517,965, on a rotating oven for concentrating sulfuric acid.

Problems

1. Let it be required that a plant producing 10 tons of 100 per cent H_2SO_4 daily be erected. The brimstone is to be shipped in by boat over the sea. How much sulfur should the contract call for, over the year, the yield being taken as stated in the text?

2. A plant manager finds that there are produced in his chamber plant 40 tons of 50° Bé. sulfuric acid every day. It would be better for his sales opportunities if that acid could be strengthened to 66° Bé. acid. Could a contact plant be erected which might take the weak acid and raise its strength to the desired one? How much sulfur would be required per day?

3. The reaction heat in the converter is 45.2 Calories for $2SO_2 + O_2 \rightarrow 2SO_3$. Compute the total heat in Btu. for a plant making 40 tons of 100 per cent H_2SO_4 per day. Conversion factors will be found in the appendix. Compare the number of pounds of bituminous coal which would generate the same amount of heat. (See Chapter 12 for the fuel value of coal.)

4. Make the same comparison of heats for the amount of sulfur burnt in the plant specified in Problem 3, if the heat evolved is $S + O_2 \rightarrow SO_2 + 69$ Calories, and the equivalent weight of bituminous coal.

5. An 86.3 per cent total SO_3 oleum may be said to be 105.8 per cent H_2SO_4, because it can be extended by the addition of water, at least theoretically, to give 105.8 parts of such acid. It is not done actually, because the reaction with water is violent; the dilution is by means of a weaker sulfuric acid. Given the same oleum, find the amount of free SO_3, and of the amount of 100 per cent H_2SO_4 it contains. Method: 86.3 per cent oleum contains 13.7 per cent water, hence $13.7 \times 98 \div 18$ parts of H_2SO_4. The corresponding amount of sulfur trioxide is bound and the remainder is free.

Reading References

"Manufacture of sulfuric acid," Andrew M. Fairlie, New York, Reinhold Publishing Corp., 1934.

"Comparison of modern chamber sulfuric acid plants," T. R. Harney, *Chem. Met. Eng.*, 36, 402 (1929).

"Europe replacing old chambers with modern high-capacity H_2SO_4 systems," Andrew M. Fairlie, *Chem. Met. Eng.*, 37, 468 (1930).

"Liquid phase operation of sulfuric acid chambers gains significance in Europe," Percy Parrish, *Chem. Met. Eng.*, 36, 68 (1929).

"Manufacture of Sulfuric Acid. Chamber Process." Vol. II of Lunge Series on the "Manufacture of acids and alkalis," W. Wyld, Gurney & Jackson, London, 1923; New York, D. Van Nostrand Co.

"Erection of huge sulfuric, nitric, mixed acid and denitrating plants under war pressure," H. E. and C. E. Hollister, *Chem. Met. Eng.*, 20, 406 (1919).

"Studies of the lead chamber process," Ernst Berl, *Trans. Am. Inst. Chem. Eng.*, 31, 193 (1935).

"Ammonia oxidation makes further gains in chamber plants," Theodore R. Olive, *Chem. Met. Eng.*, 36, 614 (1929).

"The manufacture of sulfuric acid in the United States," A. E. Wells and D. E. Fogg, *Bur. Mines Bull.*, No. 184 (1920).

"The alkali industry," J. R. Partington, of the Samuel Rideal Series, New York, D. Van Nostrand Co., 2nd ed., 1925.

"Special control apparatus in the U. S. naval sulfuric acid plant," H. Marvin Coster, *Ind. Eng. Chem.*, 23, 563 (1931).

"Purifying burner gas with electrostatic precipitators," J. J. Healey, *Chem. Met. Eng.*, 37, 366 (1930); also published with a different title in *Trans. Am. Inst. Chem. Eng.*, 24, 37 (1930).

"Characteristics of a vanadium catalyst and a new catalyst for sulfuric acid," W. W. Scott and E. B. Layfield, *Ind. Eng. Chem.*, 23, 617 (1931).

"Contact sulfuric acid converters," G. DuBois and T. R. Harney, *Ind. Eng. Chem.*, 24, 1091 (1932).

"Platinum vs. vanadium pentoxide as catalysts for sulfuric acid manufacture," A. Paul Thompson, *Trans. Am. Inst. Chem. Eng.*, 27, 264-309 (1931), with a long discussion.

"A modern contact sulfuric acid plant," Daniel S. Dinsmoor, *Trans. Am. Inst. Chem. Eng.*, 26, 158 (1931).

"Contact sulfuric acid plant," W. M. Cobleigh, *Ind. Eng. Chem.*, 24, 717 (1932), the plant of the Consolidated Mining and Smelting Co. of Canada, at Trail.

"A new contact sulfuric acid process," A. O. Jaeger, *Ind. Eng. Chem.*, 21, 627 (1929).

"The manufacture of sulphuric acid. Contact process." Vol. IV of the Lunge Series on the "Manufacture of acids and alkalis," Frank Douglas Miles, Gurney and Jackson, London, 1925; New York, D. Van Nostrand Co., Inc.

"The Manufacture of sulfuric acid by the contact process," M. F. Chase and F. E. Pierce, *Ind. Eng. Chem.*, 14, 498 (1922).

"Influence of reaction rate on operating conditions in contact sulfuric acid manufacture," W. K. Lewis and E. D. Ries, *Ind. Eng. Chem.*, 17, 593 (1925); 19, 830 (1927).

"Organic inhibitors of corrosion; aromatic amines," Charles A. Mann, Byron E. Lauer and Clifford T. Hultin, *Ind. Eng. Chem.*, 28, 1048 (1936).

"Concentration of sulphuric acid; modern plant developments," by P. Parrish, *The Industrial Chemist (London)*, 17, 41 (1941).

"Improvements introduced in Mills Packard Chambers," by Andrew M. Fairlie, *Am. Inst. Chem. Eng.*, 33, 569 (1937).

"'Chemico' drum-type sulfuric acid concentrator," J. H. Berger and A. J. Gloster, *Chem. Eng. Prog.*, 43, 225 (1947).

"Sulfuric acid concentration, Du Pont falling-film process," Francis S. Chambers and Ralph F. Peterson, *Chem. Eng. Prog.*, 43, 219 (1947).

"Concentration of sulfuric acid under vacuum," J. F. Burke and E. Mantius, *Chem. Eng. Prog.*, 43, 237 (1947).

A study of the theory for the contact process will include: "Beiträge zur Theorie technischer Prozesse. I. Bildungsgeschwindigkeit von Schwefelsäureanhydrid bei Anwesenheit von Platin," G. Bodländer und K. Köppen, *Z. für Elektrochemie*, 9, 559-

568 (1903). "II. Gleichgewichte zwischen Schwefeltrioxyd, Schwefeldioxyd und Sauerstoff," *Ibid.*, 787-794. In the same volume read also, p. 696, "Chemische Kinetik der Kontaktschwefelsäure," by M. Bodenstein, and on p. 735, on the definition of catalysis. See also: "Gleichgewichtsmessungen an der Kontaktschwefelsäure," Max Bodenstein und Wilhelm Pohl, *Z. für Electrochemie,* **11**, 373-384 (1905), in which the authors employ flowing gases over platinum.

"Modern developments in the design of plant for the concentration of sulphuric acid," P. Parrish, *Trans. Inst. Chem. Eng. (London),* **19**, 1-24 (1941).

Until recent years, the only commercial way to make nitric acid was with the aid of the non-volatile sulfuric acid, liberating the volatile nitric acid from its sodium salt. Nitric acid is now made from atmospheric nitrogen, via ammonia. Its production from natural nitrates died out some years ago, at least in the United States, but during the last 15 years it has been on the increase. From whichever source it is obtained, nitric acid is irreplaceable in the manufacture of dye intermediates and explosives. Nitrogen compounds are of the greatest importance for agriculture.

Chapter 2

Nitric Acid from Sodium Nitrate, Chile Saltpeter, Mixed Acid, Iodine, Hydrofluoric Acid, Aluminum Sulfate

Until about 12 years ago, nitric acid was made exclusively by the action of sulfuric acid on Chile saltpeter, the commercial salt of the acid. Since then, the manufacture of nitric acid by the catalytic oxidation of ammonia with atmospheric oxygen, described in full in Chapter 6, has become the standard process. A number of plants continued nevertheless to make their nitric acid from sodium nitrate and sulfuric acid, in the usual retorts, because in that way the concentrated acid, 98 and 99 per cent HNO_3, is readily obtained, while the oxidation of ammonia furnishes 50 or 60 per cent nitric acid at best. The strong acid is indispensable for the manufacture of explosives, of dye intermediates, and for most nitrations. The weaker acid may be concentrated by mixing it with sulfuric acid and then distilling; another way is to neutralize the weaker acid with soda ash, isolate the sodium nitrate formed, and treat it in retorts with sulfuric acid. The second method has the advantage of producing a by-product, nitre cake, which becomes the starting material for a number of other heavy chemicals, all of them indispensable in the national economy.

For decades Chile saltpeter was an essential material for the chemical industries; but early in the thirties, it had lost much of its earlier importance. From the earliest day of its production to the present, its main use was and still is as a nitrogenous fertilizer; on the basis of tonnage, its service as a raw material for nitric acid manufacture was secondary. A part, but only a part, of the tremendous decline was due to the world depression. Chile saltpeter lost in importance mainly because synthetic ammonium sulfate, and soon synthetic sodium nitrate, largely replaced it in world markets. In the year June 1928-June 1929, Chile saltpeter equivalent to 490,000 metric tons of nitrogen was produced; from that date on, the production declined, reaching a low of 71,000 in 1932-33. Since then, the amount produced has been rising. In 1935-36, it was 192,000 metric tons of nitrogen; in the next year, 205,000 tons, and in 1937-38, 222,500 tons. The rise in production resulted from unusual demands by the nations in a troubled world, and was helped by the introduction of an improved system for extrac-

tion of the nitrate from the ore. In the post-war period, activity has again increased. The estimated production for the year ending June 30, 1948 is 288,000 tons of nitrogen (*Foreign Commerce Weekly*, U. S. Dept. of Commerce).

Chile saltpeter is extracted from an ore found in the Terapaca and Arica districts of northern Chile, where the rainfall is so scant that the soluble salts present in the soil have not been washed away. The nitrate-bearing rock lies near the surface, under 6 to 10 feet of overburden, and extends to a depth of 50 feet. The Shanks method of extraction, the older method, is to load the rock, called "caliche" if rich, and "costra" if poor in nitrates, into carts or cars. These are pulled to the plant by mules; there the ore is crushed to a coarse size, loaded into leaching tanks and treated with hot water. A series of tanks is employed, and the extraction is countercurrent, so that a strong, hot solution is obtained from which the nitrate crystallizes on cooling. Sodium nitrate is extremely soluble in water. During the leaching, the slightly soluble sulfate is left behind with the insoluble earthy portions, and also some of the other salts present in the ore, as indicated in Table 6.

TABLE 6.—*Analysis of a typical caliche.*

Sodium nitrate	17.6%	Magnesium sulfate	3.9%
Potassium nitrate	1.3	Calcium sulfate	5.5
Sodium chloride	16.1	Sodium iodate	0.11
Sodium sulfate	6.5	Sodium borate	0.94
		Potassium perchlorate	0.23

Total salts 52.18%.

A certain amount of sodium chloride and other salts pass into the nitrate liquor; part of these crystallize with the nitrate, and part remain in the mother liquor.

In the newer Guggenheim process, the extraction is performed at 40° C. (104° F.), instead of steam temperatures. Mining and hauling to the extraction plant are performed by power shovels and cars; the ore is freed of earthy admixtures (as fines which pass out) on vibratory screens, and is then leached in an elaborate series of tanks by spent mother liquor at the temperature mentioned above. The rich nitrate liquor is cooled to 15° C. (59° F.) in interchangers against outgoing spent liquor, then to 5° C. (41° F.) by ammonia refrigeration. Sodium nitrate crystals separate to some extent in intermediate vessels with cone bottoms; most of the crystals remain suspended, and are thickened in mechanical thickeners. The slurries of crystals are centrifuged; the crystal mass is then briquetted, heated to melting in a reverberatory furnace, and the melt sprayed from nozzles to form pellets. The greater part of the mother liquor, after passing the interchangers, is used again; part of it is worked up for its iodate and potassium nitrate content. The Guggenheim system employs mechanical methods in mining and loading, and the operations in the plant are highly mechanized, so that the labor cost is low; it requires less fuel, works poor as well as rich ores, and gives a product analyzing 98.8 per cent $NaNO_3$, against

95.5 per cent for the Shanks product. The pellets are shipped in bulk or in packages. The Shanks nitrate is shipped mostly in burlap bags.

A considerable amount of Chile saltpeter is used in dynamite mixtures, as such, without any treatment.

The production of Chilean sodium nitrate in the season 1939-40 was 1,639,835 short tons, and the price $29.00 to $29.40 a ton. The estimated production for 1947/48 is 1,850,000 short tons. The price quoted for crude sodium nitrate (Feb. 1948) is $37.00 to $44.50 a ton.

Nitric Acid from Synthetic Sodium Nitrate

The reaction between sulfuric acid and sodium nitrate takes place in cast-iron retorts varying in capacity between 1500 and 5000 pounds. The nitrate is shoveled in through an opening in the front of the smaller, cylindrical retorts, or dumped into the larger, square or pot-type retorts through an opening in the top, from small trucks on rails. The sulfuric acid is run in next, and then the retort is heated gently from its own small fireplace. Nitric acid is a liquid which boils at 86° C., so that it is readily vaporized; high heat is detrimental, for it decomposes the acid. The vapors pass to a condenser cooled by water; the gases which do not condense are absorbed in water in final towers called Lunge towers. The operation of the retorts is intermittent, and for any size requires one day when working normally.

The amount of sulfuric acid is sufficient to form the acid sulfate, $NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4$; only one-half of this acid functions to liberate nitric acid, the other half remains unused. The reason for this practice is that the acid sulfate is a liquid and may be run out. Its acid content is fully utilized in the normal sequence of heavy chemical manufacture.

The amount of acid in the acid sulfate, called the nitre cake, is not 40.80 per cent, as the formula $NaHSO_4$ suggests, but 37.33, or even 30 per cent; the amounts of water vary, with a corresponding variation in the melting point, which lies between 210 and 320° F. (99° and 160° C.).[1] At the beginning of the distillation the strongest acid passes out, essentially anhydrous; near the end, a weaker acid is produced as the temperature is raised. The aim of the nitric acid maker is to produce strong acid; a certain amount of weak acid is unavoidable, for on decomposing, nitric acid itself produces water; but the amount of weak acid may be considerably reduced by using strong sulfuric acid, 98 per cent H_2SO_4, in the retort instead of the more usual 66° Bé. acid. The acid is more or less brown in color, especially the concentrated acid, because of the presence of oxides of nitrogen.

The condensation of the vapors is performed chiefly in one of two systems, the Gutmann system and the S-bend or Skoglund system. Other installations are the Hough, the Valentiner and the Uebel. The Gutmann system is illustrated in Figure 20.

Nitric acid from Chilean sodium nitrate is made in the same way as from synthetic sodium nitrate.

[1] Some further remarks on this matter will be found in Chapter 3.

Bleached Nitric Acid. It is necessary, for certain uses, to produce nitric acid free or almost free from the lower oxides of nitrogen (such as NO, NO_2). A pale nitric acid of this type is produced by the Valentiner system which includes operation under reduced pressure (one-third atmosphere); an easier way is to set up a bleacher in connection with an S-bend condenser, and operating at normal pressure; this constitutes the Skoglund system. The bleacher consists of a Duriron (or stoneware) tower about 10 feet high and 30 inches wide, set immediately behind the retort and below the condenser. The condensed acid flows down the tower, and the hot gases travel up, removing nitric oxide and dioxide from the liquid; the acid leaving the base of the bleacher is cooled by passing through a U-shaped tube set in cold water; from here it flows to the receiver. Most of the lower oxides of nitrogen reach the Lunge towers.

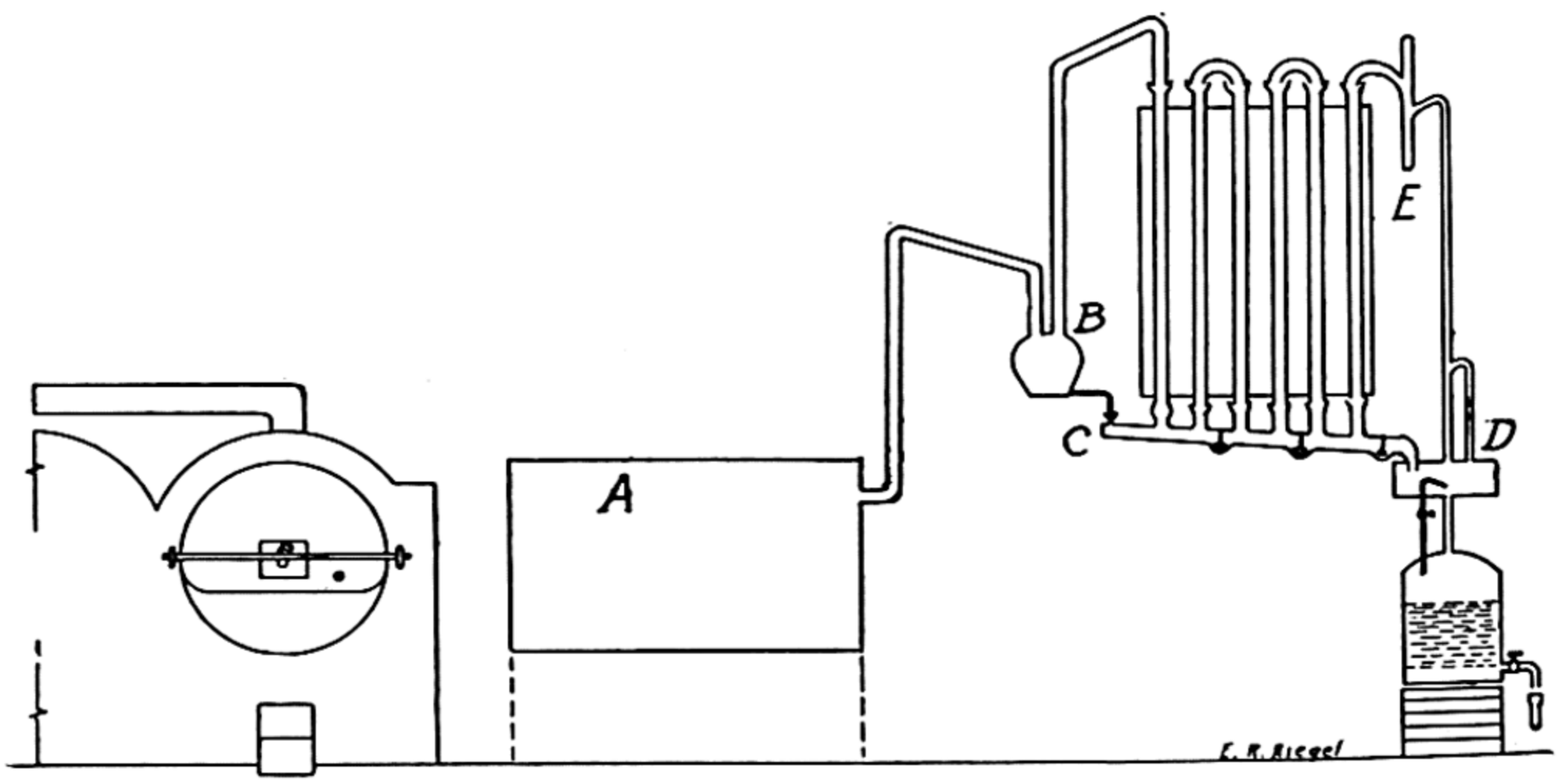


FIGURE 20.—Nitric acid from nitrates with the Gutmann condensing system. *A*, retort; *B*, collector for air-condensed acid; *C*, chamber pipe with water-cooled pipes; *D*, separator and receiver; *E*, connection to Lunge tower and chimney.

The bleacher just described serves well for strong acid, such as 98 per cent HNO_3, which usually is to be made into "mixed acid." It is sometimes desired to bleach a weaker acid, with the special purpose of making it chlorine-free. This may be done by adjusting the strength of the acid to 42° Bé. at 60° F. or 15.5° C. (67.18 per cent HNO_3), placing it in a stoneware pot set in warm water, and blowing in compressed air filtered through glass wool. A white acid results; it is suitable for manufacturers of jewelry who wish to recover gold from its copper and other alloys; it must contain no chlorine, for this would cause a loss of gold. Nitric acid made by ammonia oxidation, or from synthetic sodium nitrate, is free from chlorine.

Gas Recovery Towers. The lower oxides of nitrogen escape condensation when merely cooled; recovery towers are therefore provided in which such gases meet a trickle of water; at the same time they are oxidized, at least to a considerable extent, so that the amount of nitrous acid decreases, while that of nitric acid increases. The gas usually carries enough air for this oxidation. The original examples designed by George Lunge have

almost flat plates with perforations and ridges, so that each plate retains a certain amount of liquid, which is replaced as the liquid from above reaches it; the gas enters at the base, the water at the top. Solution of the gas takes place at each level. The strongest gas meets the rather strong solution (40 per cent HNO_3) near the base, and can enrich it somewhat; after rising to near the top, nearly exhausted, its remaining contents are abstracted by the water, as yet uncharged with acid. This tower exemplifies the counter-current principle.

The Hough system is even more compact than the Gutmann; it is made of Duriron. The Gutmann system is nearly always stoneware; the Skoglund usually has stoneware cooling pipes, which may be replaced by Duriron or silica. The Valentiner system has stoneware coils hung on a stoneware frame; these are more expensive than the simple S-bends of the Skoglund or the straight pipes of the Gutmann, so that a break is a more serious matter. The Uebel system employs three retorts working in series, and is designed for the use of weak sulfuric acid.

Nitric acid by the oxidation of ammonia is discussed in Chapter 6.

The specific gravities for the various strengths of nitric acid increase steadily, but more slowly, at the higher strengths, than the concentration.

	° Bé	Sp. Gr.	Per Cent HNO_3
Nitric acid (15° C/4° C)	36	1.33	52.34
"	40	1.38	61.24
"	45	1.45	77.24
"	47	1.48	86.01
"	49	1.51	98.05
"	49.63	1.52	99.62
"	49.654	1.5204	99.70

One hundred per cent nitric acid exists only as a solid at −41.3° C. (−42.3° F.); a certain amount of decomposition into the anhydride and water takes place on melting. Above 45° Bé., the acid is generally yellow to brown.

Nitric acid and water forms a constant-boiling mixture with maximum boiling point at 120.5° C. (249° F.), and containing 68 per cent HNO_3. On distilling a commercial acid for purification, this is the acid obtained; this has therefore become the standard strength for "C.P." acid. It is water-white. 122,596 tons of 100 per cent nitric acid were produced in 1935 in the United States, from synthetic sodium nitrate, valued at $89 a ton, or 4.5 cents a pound; in 1937, 175,860 tons, of which 140,450 tons were made and used in the same establishments, and 35,410 tons sold, at $86.20 a ton. In 1939, a total of 167,740 tons was made, of which 133,169 were made and used in the same establishments, while 34,571 tons were sold at $92.00 a ton.

During World War II, the production of nitric acid, especially of the nitrating grade, rose sharply; the production has remained fairly high in the post-war years. In 1946, nitric acid produced by all processes totaled 573,827 short tons, computed as 100 per cent HNO_3. In large lots, generally made into mixed acids, the price of nitric acid would be above $100 a ton.

Mixed Acid

In any nitration, as for instance in that of benzene, two products result: the nitrated body, here nitrobenzene, and water; as the reaction proceeds the water accumulates and tends to reverse the action. To prevent this, concentrated sulfuric acid is added; it binds the water, and permits the nitration to proceed to completion:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5 \cdot NO_2 + H_2O.$$

It has become customary to mix the nitric acid and sulfuric acid at the factory, before shipment to the consumer; this saves him one operation, and the mixture may be shipped in steel tank cars, as sulfuric acid is shipped, whereas nitric acid is usually shipped in glass. The mixture of the two acids is called "mixed acid"; it varies in the relative proportions of nitric and sulfuric acid it contains, and also in its water content, and is made to order. Examples:

Nitration of wood pulp for "fibre"	45.0% HNO_3;	48.0% H_2SO_4
Nitration of benzene	30.0	54.0
For nitroglycerin	35.6	58.0

To make mixed acid, nitric acid is raised by means of a stoneware elevator with stoneware ball valves to an upper level, and from there is fed by gravity to the mixing vessel, at about the same rate as the sulfuric acid. The mixing vessel may be a cylindrical steel tub with a paddle. Heat is evolved, which is dissipated during the slow mixing and on standing over night. In the newer plants, the mixing room is placed at a lower level than the nitric building, so that the nitric acid may be fed by gravity. The mixing is made more rapid by circulating the acid from a steel storage tank through a condenser cooled by water, and feeding the nitric acid gradually into the tank containing the charge of sulfuric acid. The circulating pump is a small steel centrifugal pump; it draws the acid from the bottom of the tank and delivers it at the top on the opposite side. The same storage tank serves as an acid egg for loading the railway tank car, which it equals in size. Mixed acid is almost colorless.

An estimate of the production of mixed acid based on its usual relation to the production of nitric acid indicates that in 1946, 171,900 tons of mixed acid were produced. The price is in the neighborhood of $56 a ton.

Iodine

Until 1931, the world production of iodine was about 2 million pounds a year, and nearly all of it was made from the mother liquor of Chilean nitrate; the price was $4, then $3 a pound. Since that date, the prospect of the complete closing down of the Chilean fields has caused a search for other sources of iodine;[2] this has been successful, and the monopoly of the Chilean producers has been broken. The domestic production was 245,696 pounds, while the imports, all from Chile, were 375,819 pounds, priced at

[2] "Fortunes and misfortunes of iodine," by P. F. Holstein, *Chem. Met. Eng.*, 39, 422 (1932).

$1.12 a pound. The price in 1935, in the United States, for domestic iodine, was $1.05 a pound; the year before, it had been $1.23.

The possible production per year from a variety of sources other than Chilean nitrate is:

	Tons	Source
Europe	140	Seaweed
Japan	150	Seaweed
Java	80	Artesian wells
United States	500	Oil wells (brines)
Russia	240	Seaweed and oil wells
Total	1110	

The iodine is present chiefly as iodide; the average concentration in brines is low (equivalent to 0.05 gram per liter), so that efficient and well-conceived processes must be installed.[3]

On the other hand it is estimated that if 500,000 tons of Chilean nitrates are produced, which is one-fifth of the normal sales, enough iodine for the world's consumption could be produced at a cost of about 50 cents a pound. The method would be the one used in the past: The mother liquor from the Chile saltpeter crystallization contains 5 grams of iodine per liter in the form of calcium iodo-chromate, calcium iodate, and some sodium iodate The free iodine is liberated by addition of sodium bisulfite solution, in the form of a solid which sinks to the bottom of the tub.[4] It is flushed into canvas bags, washed with water several times, and pressed to a cake by means of a hand press. This crude product is then distilled from cement-lined iron retorts, heated by a coal fire; stoneware pipes are fitted to each retort and in these the iodine deposits in the form of crystals containing 99 per cent or more of iodine; the moisture in the cake escapes through the loose joints in the condensing pipes. The crystals are packed in barrels holding 120 pounds, and these are wrapped in cow hides, which on shrinking form an air-tight cover which prevents the loss of iodine by sublimation The reaction is

$$2NaIO_3 + 5NaHSO_3 \longrightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2.$$

Iodine forms black, flat crystals, soluble in alcohol to a brown solution, the tincture of iodine used in the pharmacy. It serves also for the manufacture of iodoform, of aristol (di-thymol-di-iodide) its improved substitute, and of sodium and potassium iodide. It is used by the chemical analyst, in chemical laboratories in general, and for the manufacture of a few dyes; it is also used in iodized salt for table use.

The production of iodine resublimed in the United States in 1945 may be estimated as 621,000 pounds (100 per cent). There were imported in 1945 220,526 pounds, valued at $1.05. The O.P.A. price was $1.283 a pound.

Hydrofluoric Acid

Hydrogen fluoride (HF, or more correctly, H_2F_2) is a gas which is extremely soluble in water; this water solution is termed hydrofluoric acid

[3] U. S. Patent 1,944,423; 2,009,956.

[4] "The production of iodine in Chile," John B. Faust, *Ind. Eng. Chem.*, 18, 808 (1926).

Hydrogen fluoride is made by the action of sulfuric acid on calcium fluoride (CaF_2) which occurs as the mineral fluorspar in Illinois and Kentucky in the United States, and in England and other countries. The original method consisted of batch distillations from small two-piece lead retorts; this has been displaced by continuous methods, of which the following is an example.[5]

A cast-iron retort 12 feet long and 3 feet in diameter is rotated at a slow rate and heated from the outside by fire gases. At the charging end *A* (Figure 21) a mixture of powdered fluorspar and sulfuric acid of various strengths is fed in through a stationary disk, fitting by means of a sleeve into the rotating cylinder. A slight inclination causes the mass to move forward until it finally reaches the discharging end *B*. The gas and

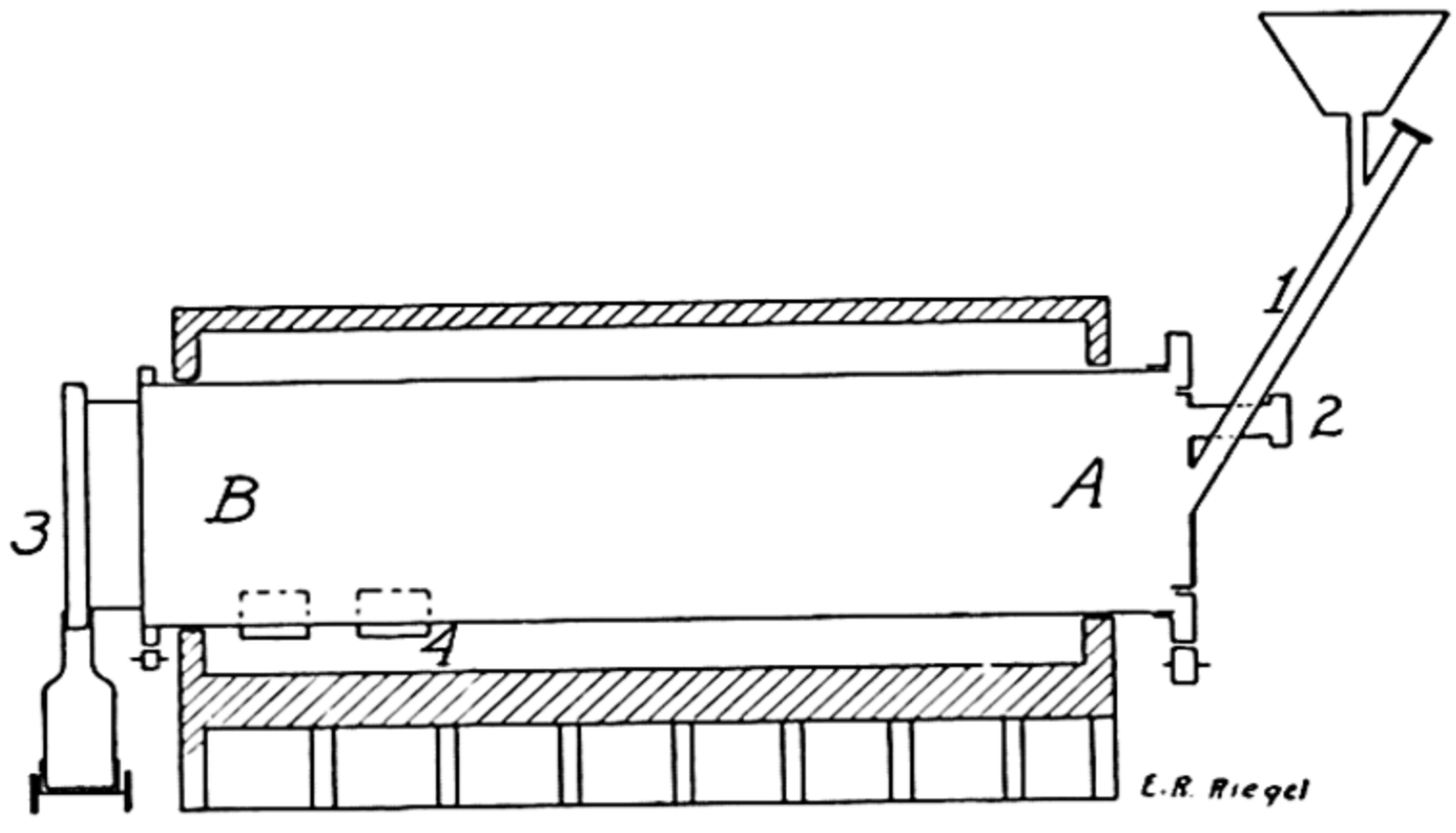


FIGURE 21.—Retort for the continuous generation of hydrofluoric acid; 1, charging pipe; 2, outlet for gas; 3, discharge ring for calcium sulfate; 4, outlet of fire gases to the flue. The retort rotates; 1 and 2 are part of the stationary disk.

moisture pass out through the opening in the stationary disk and are condensed in a lead coil. The temperature at the charging end is 120° C., at the discharging end 320° C.

The gas passes down a lead coil laid in water into a receiver, which has a charge of water and is surmounted by a small lead tower containing wetted lead trays. The amount of water is regulated to produce the desired strength.

The operation is not quite continuous, for the charging must be done at frequent intervals (30 minutes); the reason is that the mixed fluorspar and acid tend to set to a hard mass which gives off fumes of hydrogen fluoride after a few minutes. The practice is to mix the acid and mineral in small batches for 30 seconds, and introduce all of it into the retort before it can set; the evolution of the gas in the retort is fairly even. The roasted solid collects in the front end and is discharged periodically. The cylinder rotates once in about 20 seconds.

Another continuous method is that of the Rhenania Company,[6] in which sulfuric acid, as oleum, is absorbed in anhydrous calcium sulfate; with one-

[5] German Patent 262,505 (1913), to H. B. Bishop, of Brooklyn, N. Y.
[6] German Patent 355,524.

half its weight of acid the calcium sulfate is still a solid. This is mixed with finely pulverized calcium fluoride, and the resulting mixed dry charge may be fed to a muffle with mechanical plows, such as the Mannheim furnace;[7] hydrogen fluoride is evolved as a gas and dissolved in water, using lead or platinum vessels, while the roasted solid is discharged continuously and, in part, used over again. In still another proposal,[8] a great excess of nitre cake replaces the sulfuric acid.

The reaction in the case of 99 per cent H_2SO_4, as the Bishop patent recommends, is $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$. Any moisture passing over with the gas condenses in the cooling coil and remains in the acid solution. The usual commercial strengths are 30 per cent and 60 per cent HF; the 30 per cent acid is shipped in tight oak barrels, paraffin-lined; the 60 per cent acid in rectangular lead carboys 8 by 12 by 18 in., protected by a wooden box. A certain amount of the crude acid is redistilled from lead stills and shipped in ceresin wax[9] containers containing 1 pound or less. The pure acid is colorless.

The fluoride of sodium is made by neutralizing the acid by soda ash. Ammonium fluoride may be made similarly, or directly by heating together ammonium sulfate and calcium fluoride, when the ammonium fluoride sublimes and collects on the cooled cover of the retort.[10]

Since the discovery of the alkylating power of hydrogen fluoride, by Dr. V. N. Ipatieff, in the late thirties, the manufacture of anhydrous hydrofluoric acid, or 100 per cent HF, has gained in importance. The alkylation grade is made by reacting calcined calcium fluoride with sulfuric acid of a strength between 90 and 98 per cent H_2SO_4, in a Mannheim or rotary furnace as described. The escaping vapors are condensed by cooling; a yield of about 60 per cent of 95 per cent HF can be collected. Redistillation produces the anhydrous hydrogen fluoride. Pipes, fittings and valves are made of steel. In 1946, the United States production of all grades of hydrofluoric acid expressed as 100 per cent HF was 42,921,000 pounds. About 40 per cent of the total was consumed by the petroleum industry for making aviation gasoline. Anhydrous HF boils at 67.8° F. (20° C.); the liquefied gas is stored in steel tanks, and is handled in steel pressure tanks.

The chief uses of 60 per cent and less hydrofluoric acid are the making of soluble fluorides, as already stated, the cleaning of stone, and the etching of glass. Mixed with sulfuric acid it serves to remove the dull surface left by the grinding tool in cutting the design in "decorated" glassware. Anhydrous hydrogen fluoride promises to be of value as a solvent for organic substances and for inorganic salts.[11] The present price for the 30 per cent acid is 8 cents a pound, and for the 60 per cent acid, in drums, 13½ cents a pound.

Hydrofluoric acid of any strength and grade, is highly injurious to the body. The action on the skin, especially on the nails, is extremely painful and lasts many hours. Great care must be exercised in using the acid; rubber gloves and good ventilation must be provided.

[7] Chapter 3. [8] German Patent 306,567. [9] Chapter 24. [10] German Patent 94,849
[11] "Potential use of hydrogen fluoride in organic chemical processes," J. H. Simons, *Ind. Eng. Chem.*, 32, 178 (1940).

Fluorine. At one time during World War II, it became imperative that elemental fluorine, until then a curiosity and unknown to most chemists, be available in commercial quantities. In a short time, the necessary equipment had been devised. This reactive gas was generated by the electrolysis of hydrofluoric acid in the form of $KF \cdot 2HF$, a salt which with 1 per cent LiF as additive, gave a cell bath fluid at 100° C. In a carbon anode diaphragm cell, with a jacketed steel tank as the body, and with a steel cathode, it was found practical to add the hydrofluoric acid feed batchwise. The gas is freed of its 4 to 6 per cent HF content and may then be conveyed in steel or copper pipes. It may be liquefied with the aid of liquid nitrogen, or by pressure.[12] The installations were government-sponsored, and with the end of the war, all but two or three have been abandoned. Fluorine served in various capacities, among others to make uranium hexafluoride. Of late, sulfur hexafluoride has been produced commercially; it is an inert gas.

Fluosilicic acid may be made by the action of hydrofluoric acid on silica: $6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$. On a large scale, it is a by-product of calcium superphosphate manufacture,[13] in which the sulfuric acid with the fluoride impurity in the phosphate gives hydrofluoric acid gas, which reacts in part with the silica impurity giving silicon fluoride, SiF_4; the two escaping together are dissolved as a weak solution (10° Bé.) of fluosilicic acid. This may be concentrated to 13 per cent H_2SiF_6, beyond which strength decomposition occurs, with loss of SiF_4. By adding soda ash, the sodium fluosilicate is made and may be concentrated to dryness; by adding magnesium hydroxide or carbonate, magnesium fluosilicate, $MgSiF_6$, of great importance to the cement industry, is obtained. Fluosilicic acid and its salts are insecticides.

In a pre-war year, the production (U. S.) of fluosilicic acid was 3,734,000 pounds, and the price under 2 cents a pound.

Calcium fluoride may be made directly into silicon fluoride by heating it with silica in a rotating oven in the presence of magnesium sulfate; the silicon fluoride may be absorbed in a salt (NaCl) solution with the formation of sodium fluosilicate.[14]

Aluminum Sulfate

Aluminum sulfate is an important heavy chemical; it is used in paper making, in the textile industry, as a mordant for certain dyes, in the purification of river water for municipalities, and for a number of other purposes.

The production (U. S.) of aluminum sulfate, all grades, in 1945 was 587,002 short tons; "filter alum," the cheapest grade, amounted to 12,062 tons, which cost the buyer $20 a ton.

Aluminum sulfate is made by dissolving finely powdered bauxite, a naturally occurring hydrated alumina ($Al_2O_3 \cdot xH_2O$), obtained from southern France, or from Arkansas, Tennessee, and other countries (see table of

[12] A collection of 53 articles dealing with fluorine chemistry from every angle is available in *Ind. Eng. Chem.*, 39, 236-434 (1947).

[13] Chapter 7.

[14] German Patent 319,559.

production in Chapter 18), in sulfuric acid of about 50° Bé. (62 per cent H_2SO_4), to which washings from previous batches have been added. The reaction is:

$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O.$$

Several bauxite analyses follow:

	Al_2O_3	SiO_2	Fe_2O_3	Ignition Loss
Red bauxite (French)	58-60%	3- 3.5%	1-20%	20-25%
White bauxite	50-72	6-23	1- 9	20-22
Gray bauxite	56-61	7-15	1-14	21-25

Bauxite contains titanium, from a trace to 4 per cent TiO_2; it may also contain selenium.

The dissolver is lead-lined, and is provided with steam coils and a cast-lead propeller. The strong solution obtained is run to a larger tank and diluted with water sufficiently to give good settling of the undissolved matter. After settling, the clear solution is decanted, or filtered in wooden plate-and-frame presses; the bottom mud or press cake is washed with water, and the washings used in the next batch. In this diluting tank also, before running off the clear liquor, the iron salts are reduced by sodium sulfide, sodium bisulfite, or sulfur dioxide gas, from the brown-colored salts to the nearly colorless ferrous salts; they are not removed, but remain in the alum cake as ferrous salts.

The clear solution, with its iron reduced, is concentrated in a boiler until its content of alumina is 16 per cent Al_2O_3;[15] the solution is then run out into flat floor pans (steel) and let stand over night. In the morning the pan content is solidified to a white cake, with no sign of crystallization; the cake is broken by bar and chisel, reduced in a hammer mill[16] followed by a cage disintegrator[16] to a coarse powder, and barreled. The floor pans are usually 20 feet by 38 feet by 4 inches deep. In the newer plants, the pans are made a little smaller and set on a hinge so that they may be tipped when ready to dump; a hammer strikes a blow on the under side of the pan automatically when it reaches the proper dumping angle. The fractured cake drops off by gravity into a screw conveyor which feeds the hammer mill.

The preliminary treatment of the bauxite rock consists of crushing in a swing hammer mill, followed by pulverization in a Raymond suction mill.[16]

Sodic Aluminum Sulfate. One method for making sodic aluminum sulfate, $Na_2SO_4 \cdot Al_2(SO_4)_3$, is to add nitre cake to aluminum sulfate solution, purifying from lead and arsenic (by H_2S), and concentrating in lead pans; as long as the liquor is 32° Bé., not weaker, the lead from the pan is not dissolved. Concentration proceeds until the cooled mass gives a hard cake, which is crushed. All the water and most of the acid are removed in a rotary roaster, yielding a mass made up of particles the size of peas. This material is milled in a Raymond mill, and forms a very fluffy white powder, used in baking powders. On dissolving in water, it must give an acid action with bicarbonate.

[15] Crystallized aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, contains 17.35% Al_2O_3.
[16] Chapter 44.

The production of sodic aluminum sulfate and sodium aluminate combined, in 1945, was 28,943 tons, at $65.50 a ton.

Potassium alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, is made by adding potassium sulfate solution to aluminum sulfate solution, concentrating, and letting cool and harden in crystallizers with removable sides; a small amount of mother liquor flows off the crystals, which are otherwise ready for shipment.

Ammonia alum is also produced regularly; the yearly production is about 5000 tons, valued at about $55 a ton.

Oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, a crystal, is made in various ways; one of them is by the action of nitric acid on glucose from starch, in the presence of sulfuric acid. The reaction is:

$$2C_6H_{12}O_6 + 12HNO_3 \rightarrow 6H_2C_2O_4 + 12NO + 12H_2O,$$

which is made to proceed at 165° F. (73.89° C.). The oxalic acid is crystallized from the 20 per cent solution, which also contains sulfuric acid (44° Bé.). The starch is hydrolyzed in a preliminary operation. In 1946, the production of oxalic acid in crystal form was 18,467,000 pounds, valued at 10 cents a pound.

Sodium oxalate is produced on a commercial scale by heating sodium formate, which is synthesized from carbon monoxide and sodium hydroxide by the Goldschmidt process. The reaction liberates hydrogen at the same time.

$$2HCOONa \rightarrow \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$

Sodium oxalate may be dissolved in water, lime added, and the calcium salt precipitated; the latter treated with sulfuric acid forms oxalic acid which may be crystallized from the solution, after settling out the calcium sulfate.

Potassium formate may similarly be the source of oxalic acid.[17]

Problems

1. It is required to produce every working day 18,000 pounds of 98.05 per cent nitric acid, from sodium nitrate containing 98 per cent $NaNO_3$; the yield to be 90 per cent. How much sodium nitrate will be required per day, at least theoretically? This charge must be divided evenly between 10 retorts, each receiving one charge per day.

2. In Problem 1, how many pounds of 66° Bé. sulfuric acid (93.19 per cent H_2SO_4) will be required for changing all the nitrate into nitric acid? To make certain that no unwanted water will come from the sulfuric acid, it is later decided to use 98 per cent acid; in that case, how many pounds will be required?

3. Due to the decomposition of part of the nitric acid, water is formed, and only part of the yield is in the form of the desired strong acid. If for problem 1, 70 per cent of the recovered acid is in the form of 98.05 per cent HNO_3, the remainder in the form of weaker acid which must be marketed separately, how much nitrate and acid will have to be used?

4. The specific gravity of the 66° Bé. sulfuric acid in Problem 2 is 1.835; the amount required is measured in an elevated lead-lined box, one box for each retort, of which there are 10. The box is 2.5 feet × 2.5 feet, and 54 inches deep. To what height in the box (dipped with a lead stick) must the box be filled to provide the necessary amount of sulfuric acid? Weigh tanks are now being used rather than dip tanks.

5. In Problem 4, what is the weight of nitre cake furnished by the 10 retorts per day? The nitre cake will contain all sulfate radical introduced by the acid, all the

[17] U. S. Patent 2,033,097.

sodium radical brought by the nitrate, and such water as the sulfuric acid brought. The sodium nitrate should be considered anhydrous.

6. The sales department calls for 2,750 pounds of 60 per cent hydrofluoric acid per day. How many pounds of calcium fluoride must be taken, if the yield is 92 per cent, and if the calcium fluoride rock contains 90 per cent CaF_2?

7. In Problem 6, how many pounds of 66° Bé. sulfuric acid will be required?

8. The mother liquor from a Chile saltpeter crystallization is to be worked up for iodine. It contains 9.5 grams of calcium iodate per liter, and there are 28,315 liters available. How many pounds of iodine will be obtained, the yield being 89 per cent?

9. A manufacturer converts 1,000 tons of bauxite every year, containing 58 per cent alumina of which 56 per cent enters the final product, into aluminum sulfate containing "16 per cent Al_2O_3." On the alumina in the bauxite which is consumed, the yield may be considered 100 per cent. How many tons per year does he produce? How many tons for each day of a 300-day year?

10. A mixed acid is to contain 46.0 per cent HNO_3 and 46.6 per cent H_2SO_4. There is available a 49.5° Bé. nitric acid, containing 92.03 per cent HNO_3. What strength sulfuric acid will be selected, and how many pounds by weight of each will be required to make 10 tons of the mixed acid? There are shipped every week two tank cars of this mixed acid, weighing 100,000 pounds net each. How much nitric acid of the strength indicated will be required over the week, and for six working days, how many must be produced every day?

Other Patents

U. S. Patents: 1,998,106, nitric acid manufacture; 2,018,397, anhydrous hydrogen fluoride; 2,055,283, sodium aluminum sulfate, improved method of manufacture; 1,944,423, recovery of iodine from the adsorbing charcoal; 1,998,014, iodine recovered from impure silver iodide; 2,009,956, iodine extracted from natural brines; 2,212,135, production of nitric acid by compressing lower oxides of nitrogen and other steps; Can. Pat. 386,477, on concentrating nitric acid; U. S. Patent 2,189,363; on HF, U. S. Pat. 2,088,048, Brit. Pat. 554,127.

Reading References

"Technology of the Chilean nitrate industry," Harry A. Curtis, *Ind. Eng. Chem.*, 23, 456 (1931).

"Fortunes and misfortunes of iodine," P. F. Holstein, *Chem. Met. Eng.*, 39, 422 (1932).

"Manufacture of nitric acid and nitrates," Vol. VI of Lunge Series on the "Manufacture of acids and alkalis," A. Cottrell, Gurney & Jackson, London, 1923; New York, D. Van Nostrand Co., Inc.

"Freezing points of mixtures of sulfuric and nitric acids," W. C. Holmes, G. F. Hutchinson and Barton Zeiber, *Ind. Eng. Chem.*, 23, 1102 (1931).

"Freezing points of mixtures of oleum and nitric acid," H. Marvin Coster and John A. O'Callaghan, *Ind. Eng. Chem.*, 24, 1146 (1932).

"Viscosity relationships in the system sulfuric acid-nitric acid-water," F. H. Rhodes and H. B. Hodge, Jr., *Ind. Eng. Chem.*, 21, 142 (1929).

"New American iodine industry," G. Ross Robertson, *Ind. Eng. Chem.*, 26, 376 (1934).

"The production of concentrated nitric acid," A. H. Manning, *Trans. Inst. Chem. Eng. (London)*, 20, 97-103 (1942).

"Fluorine in industry" Part 1: Economic aspects of fluorspar, N. T. Hamrick and W. S. Voskuil, *Chem. Ind.*, 63, 942 (1948); Part 2: Industrial fluorine chemicals, G. C. Finger and F. H. Reed, *Chem. Ind.*, 64, 51 (1949).

In the course of manufacture of soda ash by the old Leblanc process there was discharged into the atmosphere a steady stream of hydrogen chloride; on moist days, the neighborhood of such a plant was shrouded in a fog. Laws were passed, such as the Alkali Act in England (1863) which forbade the discharge of such concentrated gases.[1] *It became necessary for manufacturers to erect absorbing towers, in which the gas was absorbed in water. The solution so obtained was the first commercial hydrochloric acid, then called muriatic acid, and became an important "heavy chemical." Hydrochloric acid is the first example of a waste product which has been saved and changed into a useful one.*

Chapter 3

Salt, Soda Ash, Salt Cake, Hydrochloric Acid, Glauber Salt, Sodium Silicate, Bromine

Salt (NaCl) occurs in nature in almost unlimited quantities. It is the direct source of such sodium compounds as soda ash, caustic soda, sodium sulfate or salt cake, crystallized sodium sulfate or Glauber salt; indirectly, through soda ash, it furnishes the sodium for sodium phosphate and many other salts. Moreover it is the source of chlorine and of hydrochloric acid. It is the uses above which come to the chemist's mind when he thinks of salt; but even without these it has an imposing list of uses, which place it among the important substances in the economic world. It serves to preserve meat, fish, and hides; it is a necessary article of diet, and as such appears on every table; it is used in dairies to give temperatures below the ice point; and it is used to thaw out switches in winter. Salt enables the soap maker to separate the soap from the glycerin lye, and the dye manufacturer to precipitate his products; in addition, salt is one of the important water-softening agents.

The form of salt used in nearly all the chemical industries,[2] in the northern part of the United States at any rate, is rock salt, cut from the solid salt deposit by means of a shaft. The shaft mines number 13 in all, distributed as follows: five in Kansas, four in Louisiana, one in Michigan, two in New York, and one in Texas. One of the New York mines is at Retsof, Livingston County; the other is at Myers, Tompkins County. The Michigan mine is near Detroit. The depth of the shafts are 1063 (Retsof), 1950 (Myers) and 1050 (Detroit). The bed of rock salt at Retsof is 18 feet thick, and 9 to 12 feet is being worked at present. The rock is lifted to the mouth of the shaft, crushed and screened to size, without any other operation for purification. The color is a light grey-white, and it is essentially pure (98.5 per cent NaCl).

The shaft of the Avery Salt Company at Avery, La., is 518 feet deep. The quality of the salt runs 99.4 per cent NaCl. There is one place at Avery Island where salt comes within 10 or 12 feet of the surface.

[1] Another Act, in 1874, prescribed that the discharge gas must not contain more than 0.0648 gram of HCl per cubic foot.

[2] Except soda ash, for which the brine is better adapted.

Salt is obtained more frequently by means of water sent down one pipe, and after becoming saturated, brought up by another pipe concentric with the first (partly by hydrostatic pressure), and then pumped to a refining plant. Such artificial brines permit a cheaper operating cost, and are well adapted to soda ash manufacture and particularly to the making of white table salt. Artificial brines are obtained in New York State at Watkins Glen, Silver Springs, Myers, and Tully near Syracuse. Artificial brines are made in Michigan, where natural brines also occur but are of less importance; one field is near Detroit (Wyandotte) and a second one in the center of the State, near Midland. Kansas has many artificial brine wells; West Virginia uses chiefly natural brines; Ohio both. A number of other states produce artificial brines.

In the dry climate of the western states, salt is found as an outcrop at the surface;[3] in some of these states this salt is utilized to some extent.

In southern California, as also in Spain and southern France, and other locations, sea water is concentrated in wide basins, by solar evaporation, until the salt deposits; by running off the mother liquors at that point, the bitter magnesium salts are removed. An interesting application of the same method is at Salt Lake, Utah. Of the many salt deposits of the world, those at Stassfurt, Germany, underlying the potassium salt beds, deserve mention because they are several thousand feet thick, compared with 18 feet at Retsof, N. Y.; the stoutest bed in America is one in Kansas, 400 feet thick,[4] while a Texas salt dome is said to be 3000 feet thick.

TABLE 7.—*United States Salt Production in Short Tons 1945.**

Manufactured (evaporated) salt	3,630,729
In brine	8,257,672
Rock salt	3,505,740
Total	15,394,141

* "Minerals Yearbook," 1945 (The rock salt production is an all-time high).

From the brines, whether artificial or natural, a grade of salt suitable for table and dairy use is made by solar evaporation (in sunny climates), by open-pan evaporation, or by evaporation in vacuum pans, with one pan (single effect) or several pans (double or triple effect); in the latter the steam raised from the salt solution in one pan becomes the heating steam in the next pan.[5] The evaporation of salt solutions offers the difficulty that, as salt is about as soluble in cold as in hot water, cooling a hot strong solution is not enough to form crystals; the water must actually be removed from the hot solution, until the salt drops out for lack of solvent.

The precipitated salt is dried in rotary driers, frequently constructed of Monel metal.

Of the 1945 output, 209,821 tons of evaporated and rock salt were iodized.

[3] From the streets of the town of Salina, Sevier County, Utah, outcrops of salt may be seen at the side of the hills; its color is red, and it may be fed to cattle.

[4] "Technology of salt making in the United States," W. C. Phalen, *Dept. Interior Bull.* No. 146, 1917, p. 124.

[5] Chapter 43.

There were 74 plants of 49 companies operating in 1945; 52 plants produced evaporated salt, 19 produced rock salt, 13 produced salt in brine.

TABLE 8.—*Production of salt by method of manufacture (U. S., 1945).*

	Short tons*	Approximate value per ton†
Evaporated salt		
Bulk		
Open pan or grainers	944,612	$ 8.65
Vacuum pans	2,001,373	7.16
Solar	442,112	2.42
Pressed blocks	242,632	10.22
Rock		
Bulk	3,410,929	3.54
Pressed blocks	94,811	8.96
Salt in brine	8,257,672	.773

* "Minerals Yearbook," 1945.
† Computed.

Pressed blocks were made by 18 evaporated salt plants and 8 rock-salt plants. The several states in the production of salt in any form stand as shown in Table 9.

TABLE 9.—*Salt (in any form) sold or used by producers (U. S., 1945)**

	Short tons	Per cent of total
Michigan	4,285,493	28
New York	2,862,224	19
Ohio	2,764,926	18
Louisiana	1,867,689	12
Texas	1,100,791	7
Kansas	855,806	6
California	694,609	4
West Virginia	370,260	2
Utah	122,997	1
Puerto Rico	12,513	0.1
New Mexico	9,980	0.07
Other States (Nev., Okla., Va.)	446,853	3

* "Minerals Yearbook," 1945.

The total world production in 1944 was estimated at over 33,000,000 metric tons, of which the United States production was 43 per cent. Germany produced 4,126,534 metric tons of rock salt, and 569,393 tons of evaporated salt, in 1942, the highest production of salt for that country in recent years. Other large producers are Canada, India, Brazil and Spain.

SODA ASH, THE COMMERCIAL SODIUM CARBONATE

In the United States, soda ash from salt is made by the ammonia process exclusively; in England, a certain amount, decreasing yearly, is made by the older Leblanc process; but even there, over three-quarters of the total production is by the ammonia process. In France, Belgium, Germany,[6] and other countries, the soda ash made is ammonia soda. To some extent,

[6] The Honigmann process produced about half the ammonia soda manufactured in Germany; it has been largely displaced by Solvay installations.

natural soda is isolated from the accompanying salts; such natural sodas and the ashes of seashore plants were the only source until Leblanc invented his process in the closing years of the eighteenth century.

The ammonia soda is usually called Solvay soda, for the successful manufacture, in 1864, by this process is due to Ernest Solvay, a Belgian, and many of the devices still in use were patented by him. The process is based on the fact that when ammonium bicarbonate is added to a saturated solu-

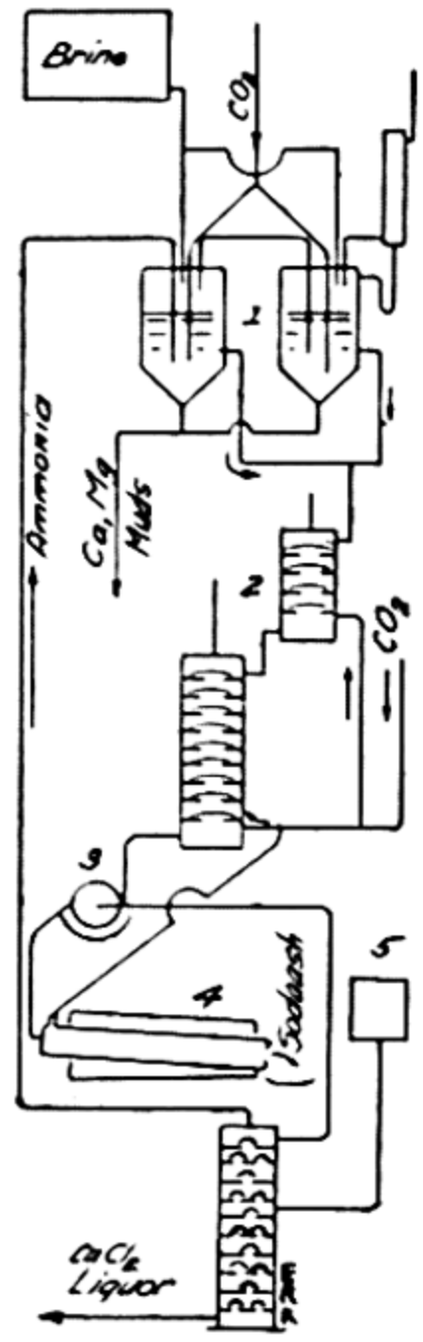


FIGURE 22.—Simplified diagrammatic flow sheet for the Solvay ammonia soda process. 1, brine tanks with ammonia absorption; 2, carbonating towers; 3, rotary suction filter; 4, calciner, giving the finished product; 5, milk of lime box for ammonia still below. The ammonia circulates. Lime kiln not shown.

tion of common salt, the ammonium salt dissolves and sodium bicarbonate separates as a solid; if filtered, dried, and calcined, it is changed to soda ash, or sodium carbonate, Na_2CO_3:

$$NH_4HCO_3 + NaCl \rightleftarrows NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 + \text{heat} \rightarrow Na_2CO_3 + H_2O + CO_2.$$

This simple principle proved difficult of application, for ammonia is comparatively expensive, and unless it is all, or nearly all, recovered, the process cannot sustain itself economically.[7] It was the nearly complete recovery of the ammonia which enabled Solvay to defeat the well-established Leblanc soda process.

In practice, a saturated salt solution is treated with ammonia gas, and this solution is then saturated with carbon dioxide; the resulting suspension of sodium bicarbonate in an ammonium chloride solution is filtered, and the sodium bicarbonate is dried and calcined. (*See* Figure 22.) The ammonium chloride filtrate is treated with lime and steam to recover the ammonia. The danger of losing ammonia in this operation is not great; it is rather

[7] The minimum amount of ammonia in process is one-third the amount of soda ash it helps make; taking the low price of 5 cents for 1 lb. NH_3, and 1½ cents for soda ash, the ammonia in process is worth as much as the material produced.

in the gas leaving the carbonating vessels and in that leaving the calcining vessel that provision must be made to recover any ammonia which it may contain.

The carbon dioxide is obtained by burning limestone, and this furnishes at the same time the lime necessary for treating the ammonium chloride solution. It is clear that much fuel is required to burn the limestone, to calcine the sodium bicarbonate, and to raise steam for the ammonium chloride still. For the reaction proper, no fuel is required.

The ammonia process has one imperfection, in that the chlorine which common salt furnishes is not recovered, except to a small extent; it passes to the sewer in the form of a solution of calcium chloride.

Ammoniating the Brine. As a rule, soda ash plants are located near the source of salt; thus the Syracuse, N. Y., plant formerly drew brines from the property, and now that a greater supply is needed, brine from Watkins Glen and the neighborhood is piped to Syracuse, about 20 miles away; the brines flow by gravity. At Wyandotte, Mich., huge deposits of salt are available. The great Dombasle plant in Lorraine, France, was also located there because of the almost limitless supply of salt in the region. Rock salt may be shipped in by rail, which, however, involves extra expense for freight, and rock salt costs more than salt in brine (see Table 8). The brine must be freed from calcium and magnesium salts, which tend to clog the carbonating towers in the later steps. This purification takes place in the same vessels in which the ammonia is absorbed. Such vessels are usually upright cylinders 15 feet high and 12 feet wide, with covers and conical bottoms. Ammonia dissolves in brine with evolution of heat, so that cooling cells hung from the cover and containing flowing cold water form part of the absorber. Towers with shelves may also be used, with cooling coils outside.

The brine run into the absorber does not fill it, as space for expansion must be left; as the ammonia gas dissolves, the volume increases. At the same time, the solubility of the salt diminishes; by feeding in dry ammonia gas, thus avoiding moisture which would dilute the brine and disturb the conditions, the desired amount of ammonia may be introduced while the salt content remains at the saturation point for that particular ammonia content.[8] A saturated salt solution at 15° C. contains 318 grams of NaCl per liter of solution, if no ammonia is present. A solution containing 60 grams of ammonia per liter is saturated with respect to salt if it contains 275 grams NaCl per liter, also at 15° C. This amount of ammonia requires only 206 grams of NaCl for the reaction, so that there is an excess of 69 grams of salt (33 per cent); because some ammonia remains as ammonium bicarbonate, since the reaction $NH_4HCO_3 + NaCl \rightleftarrows NaHCO_3 + NH_4Cl$ does not run to completion (to 73 per cent for good operating conditions), the excess salt is really somewhat greater. The excess of salt is desirable, first because it drives the reaction to the right, and secondly, because it diminishes the solubility of the sodium bicarbonate.

A certain amount of carbon dioxide gas is sent into the absorber at the same time, but not enough to form ammonium carbonate; the calcium, most

[8] Some salt may separate out as a solid, which then passes out with the settlings.

of the magnesium,[9] and all the iron salts precipitate, and collect in the cone. After the proper amount of ammonia has been absorbed, the solution is settled and the clear ammonia-brine is blown by compressed carbon dioxide to the carbonating tower. A loss of ammonia during the treatment of the brine is avoided by connecting the outlet pipe of the absorber to a small tower with shelves, down which a fresh brine solution travels. By using a battery of absorbers, a supply of ammoniated brine is always ready.

There are two sources of carbon dioxide; one is the limestone kiln which furnishes gas containing 35 to 40 per cent CO_2, the rest mainly nitrogen; the other source is the furnace in which the sodium bicarbonate is calcined; its gas may be as high as 95 per cent CO_2. This second portion of the gas may be considered as circulating. In some plants, the two gases are combined in the pump house and no distinction is made; in others, they are used as indicated farther on.

Carbonating the Ammoniated Brine. In the Solvay system, carbonation is performed in towers with shelves, on the counter-current principle; the brine flows downward, the gas enters at the base and travels upward; the other systems are gradually adopting the towers. Two towers are used in many of the plants, instead of the original single tower; a short first tower, in which enough carbon dioxide is fed into the solution to form neutral ammonium carbonate:

$$2NH_3+CO_2+H_2O\rightarrow(NH_4)_2CO_3. \qquad (1)$$

In the second, taller tower, enough additional carbon dioxide enters to form the bicarbonate:

$$(NH_4)_2CO_3+H_2O+CO_2\rightarrow 2NH_4HCO_3. \qquad (2)$$

In other plants, the tower is a single unit, and there are several towers. If there are five, to take an example, four would be actively precipitating bicarbonate; the fifth one would receive the ammoniated brine from the saturators, as well as a moderate flow of lean gas (40 per cent CO_2), delivering at its bottom outlet a clear liquor, carbonated as required by reaction (1). The temperature is allowed to rise, reaching 32 to 40° C. [90 to 104° F.]. The partly carbonated ammoniated brine is an active solvent for incrustations of bicarbonate, which form in spite of the engineers' skill. This procedure then has as object (1), the partial carbonation of the ammoniated brine, (2), the removal of the crusts. Each tower in turn works four days, and on the fifth, it is rid of all obstructions. From the fifth tower, the clear liquor is divided and fed in equal amount to each one of the four working towers. The flow of brine through the fifth tower is four times faster than its flow through the working or precipitating tower.

[9] A magnesium salt content in the brine is not desired, and yet if the amount is small, and it escapes precipitation by the ammonia, which occurs because ammonia is a poor reagent for the purpose, its presence may be an advantage. Magnesia forms glass-like double salts with NaCl, which coat the walls of the apparatus, and prevent the contamination of the soda by iron with its subsequent discoloration. The factory experience is that those plants which occasionally have their soda colored red (unsalable) operate with magnesia-free brine.

On traveling down the working tower, the liquor meets a flow of strong carbon dioxide gas, traveling upward. Reaction (2) takes place, and simultaneously, reaction (3).

$$NH_4HCO_3 + NaCl \rightleftarrows NaHCO_3 + NH_4Cl \qquad (3)$$

The temperature rises to 65° C. [149° F.]; by means of the cooling pipes provided in the lower sections of the tower (see Figure 23), the temperature may be lowered. It is essential not to lower it too far, however, for at low temperature the sodium bicarbonate forms in such finely divided form that it cannot be filtered. The temperature of 26 to 27° C. [78.8 to 80.6° F.] has been found to be right for the production of grains of the proper size.

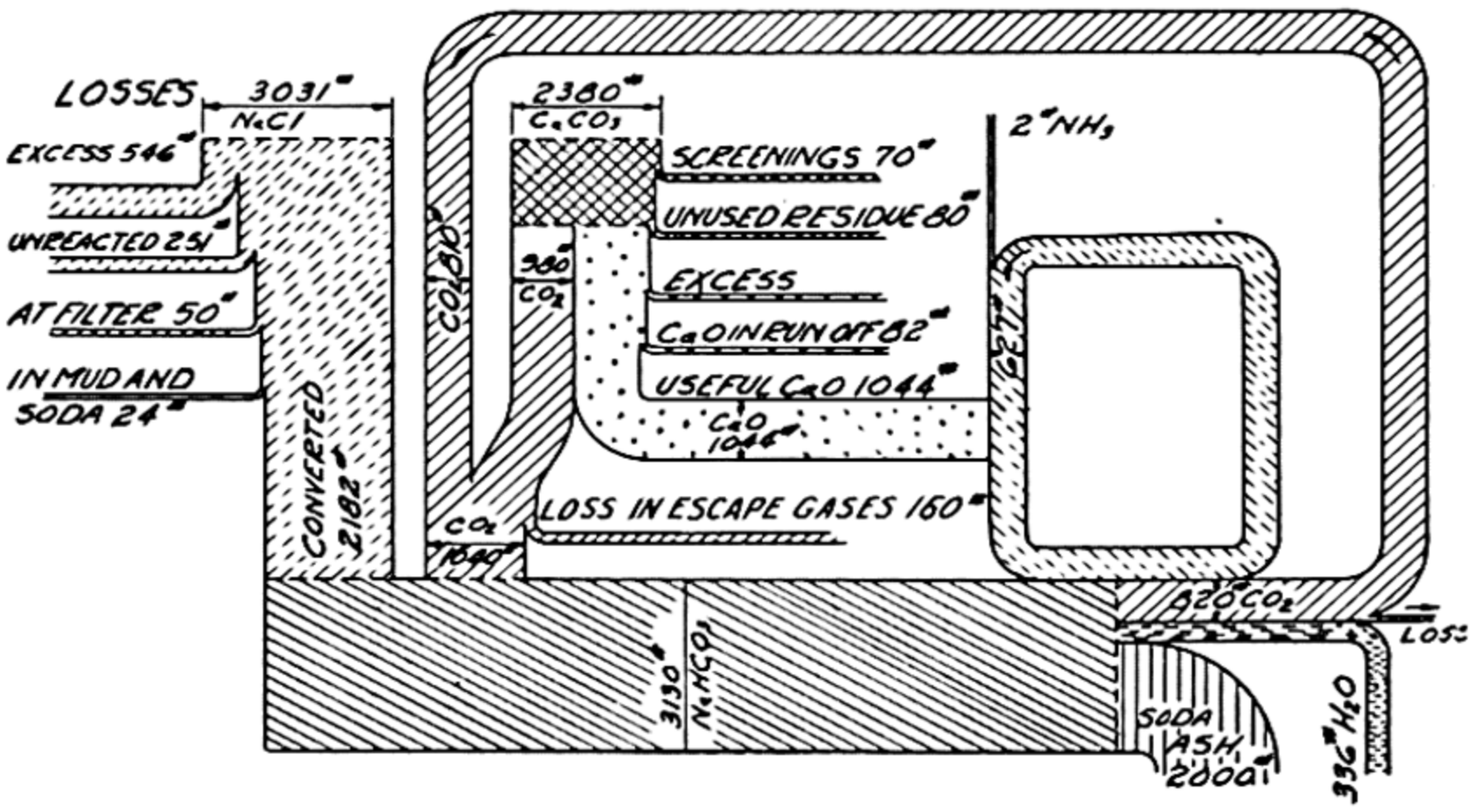


FIGURE 23.—Diagrammatic sketch of the amounts of raw materials, circulated chemicals, products and discards in the Solvay process for soda ash. The widths of the columns and frames are in proportion to the weight of the materials they represent. (*After Kirchner.*)

The tower consists of 28 upper sections, each 15 inches high, surmounting 9 lower sections which are 42 inches high. The material is cast iron. Each upper section has a floor with central opening, over which a dome-shaped piece is supported by three brackets. The rising gas is deflected sidewise by the domes. The lower sections have nests of cooling tubes; for the latter, wrought iron has proved a little more durable than cast iron. Other details may be obtained from Figure 24. In may be well to point out that this tower is not a bubble tower; the rising gas has no liquid seals to overcome; it meets only the rain and foam of the descending liquid or slurry. Each shelf is flushed clean of deposit (within limits) by the descending liquid.

A tower such as that shown in Figure 24 has a capacity of 50 tons of finished soda per day.

The brine containing 60 grams of ammonia per liter requires 83 grams of carbon dioxide to form the neutral carbonate, a part of which is added in the absorbers. For the bicarbonate, an additional 83 grams must be added; in fact, a little more is required, for some carbon dioxide passes out unused from the top of the main tower. It carries away some ammonia,

which is recovered with part of the carbon dioxide, in a supplementary tower fed with fresh brine.

The carbon dioxide gas enters at the base of the tower under a pressure

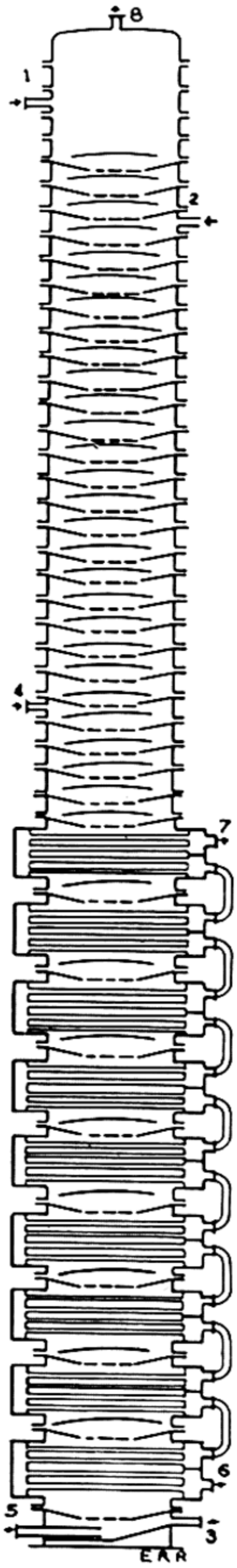


FIGURE 24.—A carbonating tower in the ammonia soda process (Solvay); it is 69 feet high, and 6 feet in diameter.

1. Entry for ammoniated brine, used when the tower is being cleaned.
2. Entry for the ammoniated brine for the regular bicarbonate precipitation.

3 and 4. Carbon dioxide entries.

5. Outlet for the bicarbonate slurry.
6. Cooling water inlet, and
7. Its outlet.
8. Escape for uncondensed gases.

The supports for the domes not shown. (Modeled after Kirchner.)

of 30 pounds. As it rises, much of it is absorbed and the pressure drops. At the top of the tower the unabsorbed portion and the inert gas (nitrogen) pass through a supplementary tower where fresh brine removes any ammonia carried out.

The suspension is drawn off from the lowest compartment at frequent intervals, and fed to the trough of a continuous suction filter, of either the drum or the single-disk type. The cake is washed to remove all ammonium chloride; at the same time about 10 per cent of the bicarbonate is also dissolved and lost. In spite of the washing some ammonium bicarbonate is left in the cake, and its ammonia must be recovered; this is easily done, fortunately, for the ammonia passes out with the carbon dioxide on calcining the sodium bicarbonate, and the two gases together are sent to the carbonating tower.

Calcining Sodium Bicarbonate. A great variety of devices is used for calcining the bicarbonate, which is by no means an easy operation. In Europe a covered pan with semicircular cross-section and scrapers having a sidewise motion (Thelan pan), with outside firing, is much used. In America, the rotary furnace with horizontal axis, with outside firing, is favored; to prevent the forming of insulating crusts on the walls, some of the hot cake just discharged is mixed with the cake to be calcined. The gas is saved in all cases, and forced into the carbonating devices:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

The discharged cake is light; for many uses, a denser cake is demanded; by calcining at a higher heat, the density is raised, but the dense soda ash of commerce is made by adding water to the light soda, and recalcining.

An analysis of a good commercial soda ash made by the ammonia soda process follows:

	Per Cent
Na_2CO_3	99.50
NaCl	0.20 to 0.25
Na_2SO_4	0.02
Insoluble	0.02
Moisture	balance

There is a tremendous sale for the bicarbonate to be used for baking powders, but for this purpose, the material must be purified, chiefly of ammonium salts. The crude sodium bicarbonate may be recrystallized, or a solution of soda ash may be carbonated. In 1946, 188,945 tons of refined bicarbonate were produced.

There is also a market for crystallized sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, called sal soda, made by cooling a solution of purified sodium carbonate of the proper concentration. The annual production is not far from 40,000 tons.

Ammonia Recovery. The bulk of the ammonia is present as ammonium chloride, NH_4Cl, in the filtrate from the bicarbonate; some ammonia is present as carbonate, carbamate, and bicarbonate. The recovery is performed in a modern ammonia still, such as the one shown in Chapter 14, in which the free ammonia (carbonate, sulfide) is driven off first, and then only is lime added to liberate the fixed ammonia (sulfate, chloride):

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O.$$

The calcium chloride passes out at the bottom of the still.

The run-off from still or tower contains no ammonia, or only a trace;

it is blown by steam pressure to compartment settling tanks, and there settled; the clear liquor is removed, and the semi-solid lime mud carted to the dump.

The ammonium chloride liquor contains about one-third of the original salt (NaCl) unchanged; it is better to waste it than to have a less complete reaction. Part of the calcium chloride formed is wasted; but part of it is made into a concentrated calcium chloride liquor, the "brine" of the refrigerating plants; the diluted solution is also used to sprinkle on dirt roads.[10] A considerable portion of the calcium chloride formed is evaporated to dryness, and used as stated below under Natural Calcium Chloride.

A lime kiln which allows the recovery of the carbon dioxide is used (Chapter 9). The gas from such a kiln contains the fire gases as well as the carbon dioxide from the limestone, and also dust. It is passed through a three-tray box, where it meets running water; the dust deposits, and the gas is cooled. From here it is forced into the carbonating tower.

Natural soda occurring mixed with sodium chloride and sulfate as well as magnesium salts may be isolated by treating the solution with carbon dioxide; sodium bicarbonate precipitates, is filtered off, and calcined to soda ash in horizontal rotary cylinders.[11]

The production in the United States in 1946 is given in Table 10.

TABLE 10.—*Production of soda ash in the United States.**

	1946 Short tons
Soda ash, ammonia soda process	4,284,231
Natural soda ash	209,411

* "Facts for Industry," Department of Commerce.

The 1947 production of soda ash is estimated at about 10 per cent more. The estimated distribution of soda ash for 1946 is given in Table 11.

TABLE 11.—*Estimated distribution of soda ash in the United States.**

Consuming Industries	1946 Short tons
Glass	1,400,000
Caustic and bicarbonate	1,128,000
Other chemicals	910,000
Pulp and paper	190,000
Non-ferrous metals	140,000
Cleansers and modified sodas	125,000
Soap	120,000
Water softeners	90,000
Textile	77,000
Petroleum refining	20,000
Miscellaneous	223,000
Export	67,000

* *Chem. Eng.*, 55, 106 (Feb., 1948).

The price of soda ash in 100-pound paper bags, carload lots, in 1946 was $25.60 a ton; the quotation in May, 1948 was $27.60 a ton. The

[10] Calcium chloride is hygroscopic and retains enough moisture to lay the dust.

[11] The sesquicarbonate of sodium, often mentioned in the literature on natural soda, is $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, and is also called "trona."

natural soda ash reported above was produced from brines from Owens Lake and Searles Lake, in California. Its value was above that of the previous year, 1945, which was $15.60 a ton.

Natural Calcium Chloride. The mother liquor from salt crystallization contains mostly calcium and magnesium chloride. Most of it is concentrated to a high salt content, and then "flaked" on a flaking machine. The product is packed in multi-paper bags and serves in the treatment of roads, coal and coke for dust prevention, on tennis courts, for refrigeration, and a variety of other purposes. In 1945, 218,320 tons of this calcium-magnesium chloride valued at $8.35 per ton were produced from natural brines in the United States.

A portion of by-product calcium chloride in the ammonia soda process is marketed in the form of flakes, and used for similar purposes. In 1946, calcium chloride production, which includes the chloride used in the liquid (solution) form as well as the flakes, estimated from its relation to the soda ash production, came to 557,000 tons. Calcium chloride flaked (usually 77-80 per cent $CaCl_2$), varied in price from $18.50 to $38 a ton (bags) in carload lots.

Salt Cake

Salt cake, the commercial anhydrous sodium sulfate, was produced originally by the action of sulfuric acid on salt (NaCl) in the pot and muffle process; within the last thirty-five years, the use of nitre cake instead of free acid with the salt, and the roasting of the mixture in mechanical salt-cake furnaces, has rendered the first process obsolete. It was partly to consume the nitre cake which at one time glutted the market that the mechanical salt-cake furnace was developed. It has been a brilliant success. As Chilean nitrate came to be used less, and the air oxidation of ammonia for nitric acid replaced it, less nitre cake became available. Fortunately, one of the two methods for making concentrated nitric acid from the 65 per cent acid normally produced by the oxidation of ammonia method consists of neutralizing the weak acid with soda ash and evaporating to dryness, which gives synthetic sodium nitrate. The nitrate so obtained takes the place of the earlier Chilean nitrate for the production of concentrated nitric acid, with the now desired nitre cake as by-product. The latter is then used for the mechanical salt-cake furnace operation, producing hydrochloric acid and sodium sulfate.

Another way to help matters is to make nitre cake from salt and sulfuric acid in cast-iron retorts:

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4.$$

Such nitre cake, which has never seen nitre, may be mixed with salt and fed to the mechanical furnace just as well as true nitre cake. The amount of hydrochloric acid produced, let it be noted, is twice as great, and a market must be available for the additional amount. Less salt cake, with respect to the salt used and hydrochloric acid made, is produced when starting with sulfuric acid than when starting with nitre cake from the nitric acid still, for this nitre cake is already half salt cake.

Finally, a third procedure may be adopted. The mechanical furnace may be fed with salt (NaCl) and sulfuric acid directly, and the mass plowed and heated until the reaction to the sulfate is completed:

$$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4.$$

In several important installations which have adopted this procedure, the cast-iron muffle floor has a center of acid-resisting bricks, to minimize the corroding effect of the acid.

The Mannheim Mechanical Salt-Cake Furnace

The best known mechanical furnace is the Mannheim.[12] It is an automatic device, with continuous operation; the labor is a minimum; and the labor of pulling out the fuming salt cake by hand rakes, a suffocating operation, is rendered unnecessary. When using nitre cake, the reaction is:

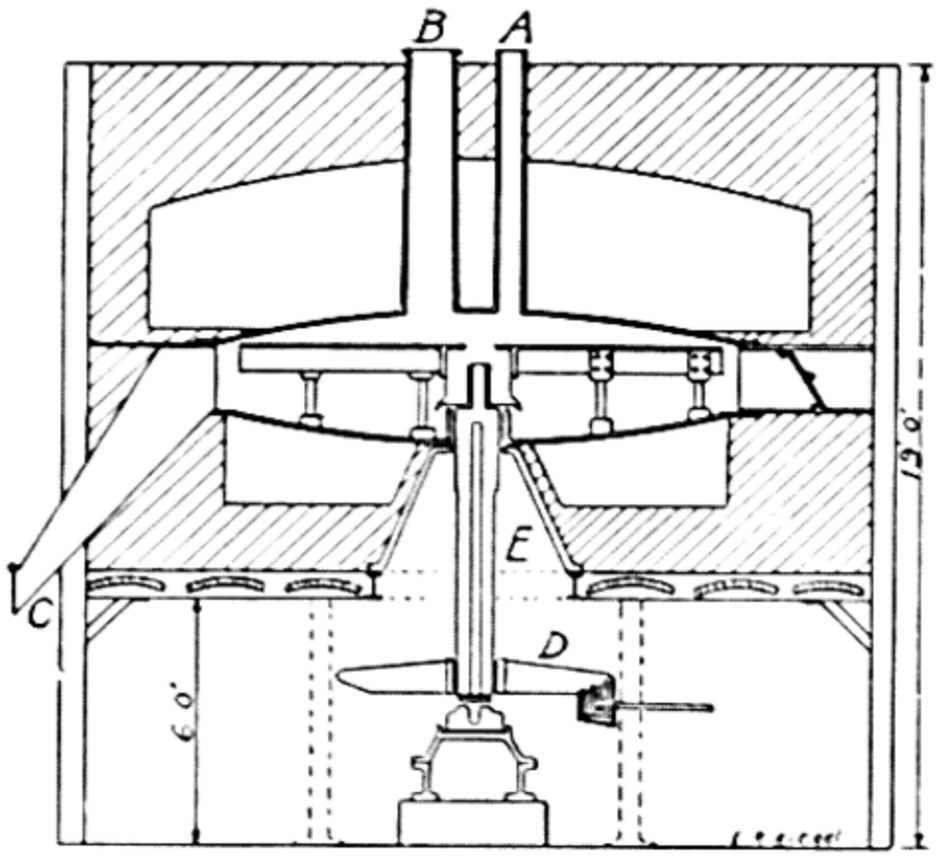


FIGURE 25.—Mannheim mechanical salt-cake furnace, with hydrogen chloride as by-product. The charge enters at *A* and is discharged at *C*; the gas passes out at *B*. The eight plows are rotated from below, by gear *D*; the shaft may be water cooled at *E*.

$$NaCl + NaHSO_4 \rightarrow HCl + Na_2SO_4.$$

It takes place to near completion at 650° C. (1202° F.).

The Mannheim furnace consists of a circular muffle of cast iron, 12 feet in diameter, with bottom and top dish-shaped; the inner height at the circumference is 20 inches, in the center 40 inches. A shaft penetrates it from below and carries four arms, each of which carries two cast-iron plows. The shaft is rotated slowly, 1 revolution in 2 minutes, by the gear and pinion indicated in Figure 25. The mixed salt and nitre cake is fed in from the top near the center, and is moved to the circumference by the plows. Plow 8 is wider than the others, and discharges the burned cake (now salt cake) through the opening of the chute (Figure 26). Here the cake accumulates to some extent and is removed in small trucks to the storage bins. The discharge cake is yellow and turns white on cooling.

Some of the details of construction of the muffle will be plain from the illustrations; the bottom and top are single castings. The sides consist of twelve curved castings which, when assembled, provide three doors; one of these is over the discharge opening and chute. Each plow differs in

[12] German Patent 137,906 (1900), Mechanischer Calcinirofen, by the Mannheim Verein.

length of shank; and each is slightly turned so that the cake is swept outward. The heat is furnished by a small fireplace. The fire gases enter over the muffle, heating the top; then travel to the under side by a passage in the brickwork and heat the lower side; from here they pass out to the chimney. (*See* Figure 27.) The temperature is registered by a platinum resistance pyrometer[13] placed in a protecting cast-iron tube reaching into the center of the muffle from above.

The salt used is rock salt, of the fineness of sand; it may be either purchased in that form, or if coarser, reduced in a swing hammer mill.[14] The nitre cake, in pieces 1 foot across or smaller, is fed to a pot crusher[14] or jaw crusher[14]; the product, the size of walnuts, is reduced to a coarse powder

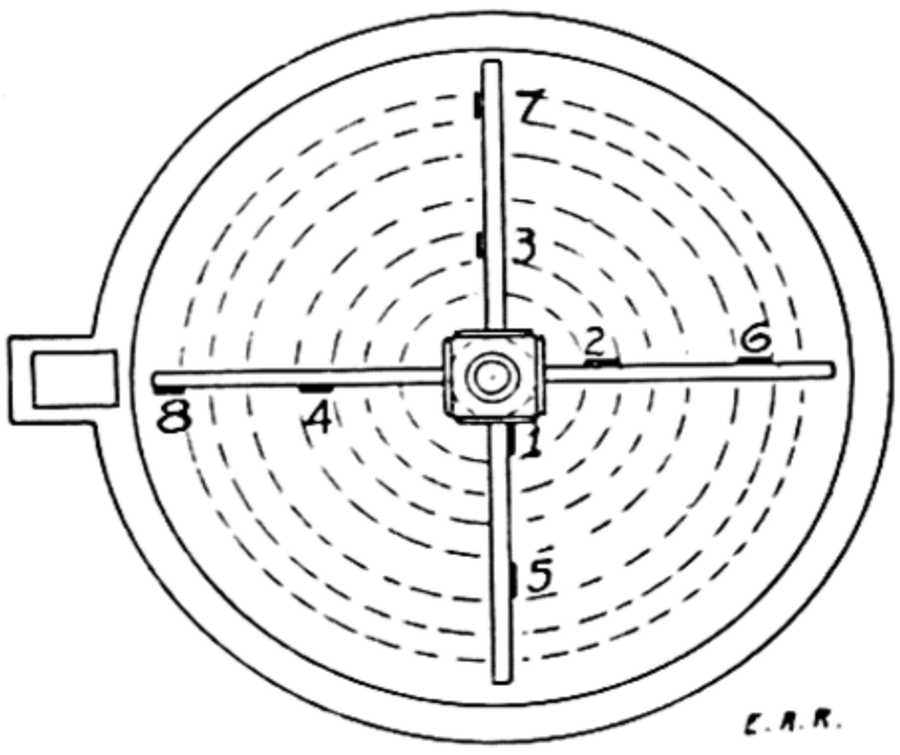


FIGURE 26.—Cross-section of the Mannheim furnace, showing bottom casting, the eight plows, and the lanes which they sweep.

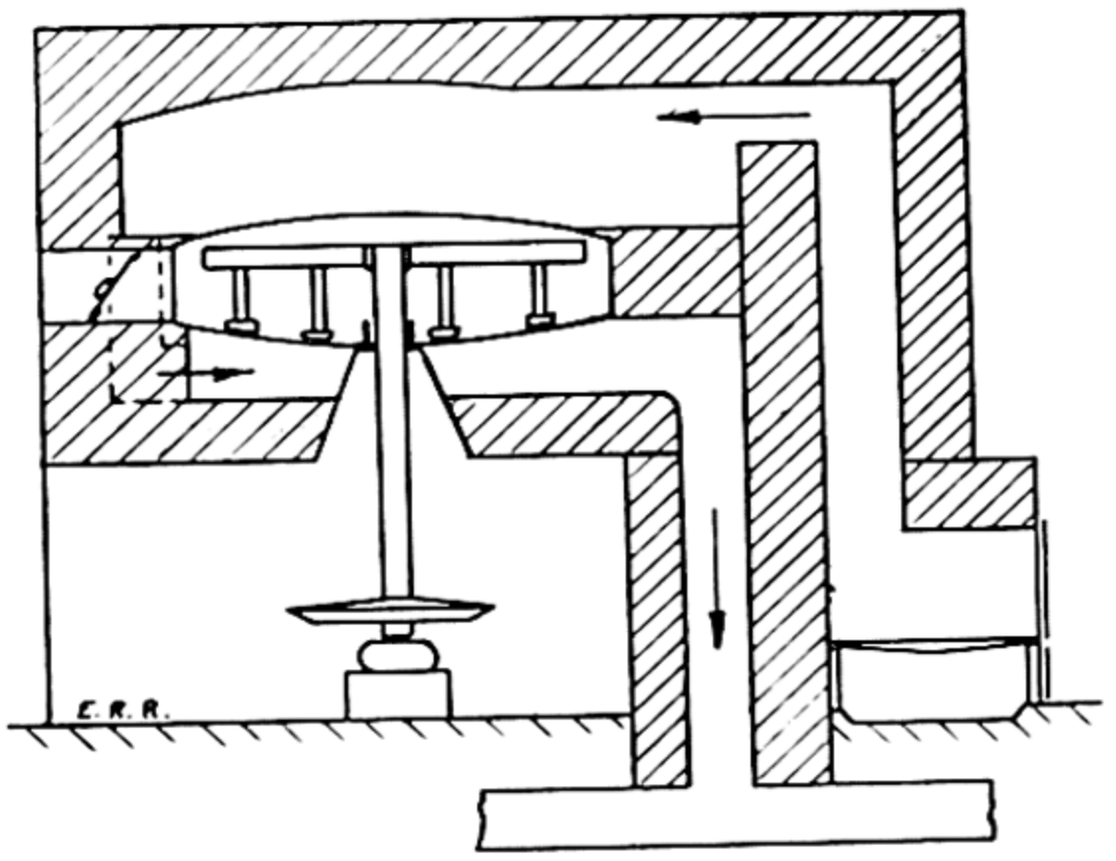


FIGURE 27.—Circulation of the fire gases around the Mannheim furnace.

in a squirrel-cage disintegrator[14] or a swing hammer mill. Salt and nitre cake are carefully mixed in some plants by placing equivalent quantities (250 pounds of salt and 700 pounds of nitre cake, for example) in a rotating cylinder and mixing for 15 minutes. In other plants merely dumping salt and nitre cake alternately into the hopper serving the screw conveyor which brings the cake to the feed pipe of the muffle is found to give sufficient mixing.

The reaction is preceded by a fusion; the nitre cake fuses first. The effect of high sulfuric acid on the fusion point of nitre cake is not so great as that of the moisture content; 10 per cent moisture lowers the fusion point from 320° F. (160° C.) for the dry cake with 37 per cent H_2SO_4 to 210° F. (99° C.); but 10 per cent sulfuric acid added to the dry nitre cake has almost no effect on its fusion point.

Temperature and Capacity. The temperature of the muffle is indicated by the pyrometer and is not kept constant, but is increased slightly as the wearing of the plows progresses; it lies between 625° and 675° C. The guide is the daily analysis of the salt cake. A well burned salt cake should contain 2 per cent or less of NaCl, and 1.5 per cent or less of H_2SO_4; if the cake runs higher in both impurities, the temperature may be increased. Other

[13] Chapter 46. [14] Chapter 44.

ways to control the quality are to change the relative proportions of salt and nitre cake, and the absolute weight fed in. In the 12-foot diameter muffle, six tons of good cake may be produced per day.

Length of Run. The plows need renewing every two months (approximate figure); the bottom casting may last two years, but one year is considered fair enough; the top casting and the sides will outlast several bottoms. The life of the plows may be lengthened by making the blades of Duriron[15] and bolting them to cast-iron shanks.

Safety Flange. Should a plow become jammed against some foreign object a break may occur in the gears, which would be an expensive accident. This is prevented by fitting the pinion shaft with two flanges working through a pin whose size is just sufficient to carry the load. Any sudden resistance will break it, and at the same time indicate that the obstruction must be removed.

Pot Stills. The nitre cake from the nitric acid retorts is supplemented, as already suggested, by the product obtained as still residue when salt is treated with sulfuric acid in the proportions indicated by the reaction:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl.$$

A mechanical furnace, differing from the Mannheim, which has been installed in American plants is the Laury furnace, a two-stage cylindrical furnace,[16] not unlike the cement furnace, but shorter and stouter.

The production of salt cake in 1945 was 660,402 tons, including the figure for Glauber Salt (see page 74); refined anhydrous sodium sulfate was 83,201 tons, while natural sodium sulfate came to 178,196 tons, a total of 838,598 tons of domestic origin. In 1946, salt cake production amounted to 527,746 tons, refined anhydrous sodium sulfate to 122,573 tons, and Glauber Salt, not included in the salt cake figure this time, to 167,153 tons as $Na_2SO_4 \cdot 10H_2O$—a total of 817,472 tons. The crude salt cake, in bulk shipments, was quoted at $15.00 in 1945 and 1946. Natural sodium sulfate in 1945 was quoted at $8.50 a ton. The present listed price (May, 1948) is $25.00 a ton for crude salt cake. A considerable tonnage of salt cake, which has fluctuated over the years, is imported.

The uses of sodium sulfate are indicated in Table 12.

TABLE 12.—*Estimated end-use distribution for sodium sulfate, 1946.**

Paper and pulp	710,000
Textile	75,000
Glass and ceramics	50,000
Heavy chemicals	50,000
Other	45,000
Total (incl. imports)	930,000

* *Chemical Industries.*

It is evident that 76 per cent of salt cake consumption is in the manufacture of kraft pulp and paper. It also forms part of the batch for window and container glass; it is the raw material for Glauber Salt, sodium sulfide,

[15] Chapter 45.
[16] U. S. Pat. 1,435,930 (1922).

and sodium thiosulfate. An important new use is as a diluent in synthetic detergents which are to be kept at about 33 per cent active strength.

Natural sodium sulfate is sulfate obtained from natural brines such as those at Searles Lake; other plants are at Brownfield, Texas; Rawlins, Wyoming; and Monahans, Texas.

Synthetic Salt Cake. The stoppage of importations of salt cake from European countries, particularly from Germany, by World War II created a shortage so serious that a synthetic salt cake was manufactured. It consisted of sulfur melted into soda ash, and was made as follows: As the soda ash leaves the calciner and enters a screw conveyor, sulfur in powder form is added. The hot ash melts the sulfur, and the action of the conveyor mixes the two, the sulfur coating the granules of soda ash, and producing a gray mass. This proved just as satisfactory in the kraft paper industry as true salt cake.[17] The production was at a rate of 400 tons a day in 1941.

The Leblanc Process for Soda Ash. In the Leblanc process,[18] salt is treated with sulfuric acid, giving sodium sulfate and hydrogen chloride; this first step was retained for the manufacture of hydrochloric acid with sodium sulfate as a by-product. The salt cake (sodium sulfate) mixed with limestone and coal is heated in a short rotary furnace, producing the "black ash" which, after leaching with water, gives a solution of sodium carbonate containing also caustic. This solution is evaporated by the waste heat of the black ash furnace, during which process it receives enough carbon dioxide to form all carbonate. The monohydrate $Na_2CO_3 \cdot H_2O$ separates, and is dehydrated completely in reverberatory furnaces. A part of the soda ash was made into caustic soda by treating the solution with lime, so that a lime kiln usually formed a part of the plant. The Leblanc process, even though no longer practiced, is one of the most famous in industrial chemistry. In the course of its development, fundamental engineering principles were recognized and firmly established (the counter-current principle, for example, in the Shanks system of lixiviation).

Hydrochloric Acid

Hydrochloric acid is made (1) from salt, in salt-cake furnaces; (2) by burning electrolytically produced chlorine in excess hydrogen; (3) as by-product from the chlorination of hydrocarbons such as pentane and benzene:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl.$$

A fourth method[19] employs chlorine and steam over heated coke (350° C.; 662° F.) containing iron compounds as catalysts, or charcoal, to which iron oxide has been added.

$$2H_2O + 2Cl_2 \rightarrow 4HCl + O_2$$

[17] Read for example: "New ideas on use of salt cake in kraft pulp process," by Walter L. Savell, *Paper Mill and Wood Pulp News*, December 9, 1939.

[18] Invented during the period of the French revolution, by Nicholas Leblanc, a physician. The inventor did not receive the promised prize from the government, and his plant suffered from the political upheavals. For a century, civilization has enjoyed abundance of window glass and inexpensive soap, thanks to Leblanc's genius, but he himself died unrewarded, unthanked, in an asylum, by his own hand. See Hou, "Manufacture of Soda," 2nd ed., Chapter 1, New York, Reinhold Publishing Corp., 1942.

[19] German Patent 427,539 (1926); *see also* "Manufacture of hydrochloric acid from chlorine," Wilhelm Kirschkind, *Ind. Eng. Chem.*, 17, 1071 (1925).

Hydrogen chloride is a gas; on cooling to room temperature, it does not condense to a liquid, as does nitric acid, but must be dissolved in water. The ordinary commercial strength is 20° Bé., at 60° F. (15.5° C.), containing 32.46 per cent HCl. The system for absorption is essentially the same, whichever method for the production of hydrogen chloride is employed. As an example, the gas from a Mannheim furnace may be taken.

The gas from the Mannheim furnace passes through a 10-inch stoneware line, coated with tar to close the pores, to a short stone box, where it cools further and deposits most of the sulfuric acid which it carries. From the stone box, it passes to S-bend coolers or to Cellarius vessels set in running water; the cold gas then passes to the absorbing towers, where the solution in water or weak acid takes place. Tower No. 3 receives cold water, and delivers at the base a 12° Bé. acid, which is warm; before feeding it to No. 2, this acid passes through about 6 lengths of 1-inch glass tubing set in cold water. The cold acid is elevated to the top of No. 2 by a small automatic, hard-rubber-lined elevator, or by a "monte-jus,"[20] a gentle stream of air into a 1-inch glass pipe so that it forms gullets of liquid which give a broken column easily pushed up. The acid solution from the base of No. 2 is cooled and fed to No. 1, where its maximum strength is obtained. The acid from No. 1, after cooling, is the 20° Bé. acid ready to ship. The daily production of a furnace furnishing 6 tons of salt cake is about 9000 pounds of 20° Bé. acid.

The towers are made of stoneware, usually in 10 sections, each 30 inches high, and 36 inches in diameter; the packing is coke of carefully selected sizes, or 3-inch spiral rings of stoneware. Three towers are sufficient for complete absorption, but in many plants four are used, and in the summer months, even five.

The gas is pulled through the absorbing system by a fan set at the exit from the third tower. (*See* Figure 28.) The fan is protected from acid mist by a small coke box, so that a lead-lined fan or even an ordinary steel fan may be used. The suction exerted on the system is so regulated that it is felt at the muffle just enough to prevent the gas from passing around the working doors into the room. The strong gas may also be propelled by a stoneware fan set between the cooler and the first tower.

The stone box is built of sandstones which have been boiled in tar to prevent the acid from penetrating them; the stones are held together by cast-iron corner pieces and rods. The joints are made tight with rubber gaskets, or with asbestos cord smeared with china clay and linseed oil. The cooler may be made of S-bends, stoneware or fused quartz; for one furnace, there would be 5 rows of 4-inch S-bends, of which one is shown in the illustration; these pipes are cooled by a small amount of water trickling over them.

In some installations the towers are supplemented by Cellerius vessels of stoneware, about 46 inches long by 28 inches across, for acid cooling and adsorption (*see* Figure 29). The design of this vessel provides for maximum absorption surface to a given total volume of solution. The function of the cooler S-bends may be performed by the Cellarius for gas cooling, of the

[20] *Monte-jus* is French for juice-raiser.

same dimensions as just stated, but constructed in the opposite sense, so that it holds no liquid. Figure 30 indicates the details.

Acid made by method (3) involves the removal of any unchlorinated hydrocarbon present in vapor form, then absorbing hydrogen chloride in water in a continuous system. For the recovery of hydrochloric acid obtained as by-product of pentane chlorination, a plant has been described.[21]

Acid made by method (2), namely by burning chlorine in hydrogen, absorbed in towers with iron-free packing, is a water-white acid, essentially chemically pure. It more than meets the requirements for the chemist's C. P. acid. A patented method[22] avoids an excess of hydrogen with the

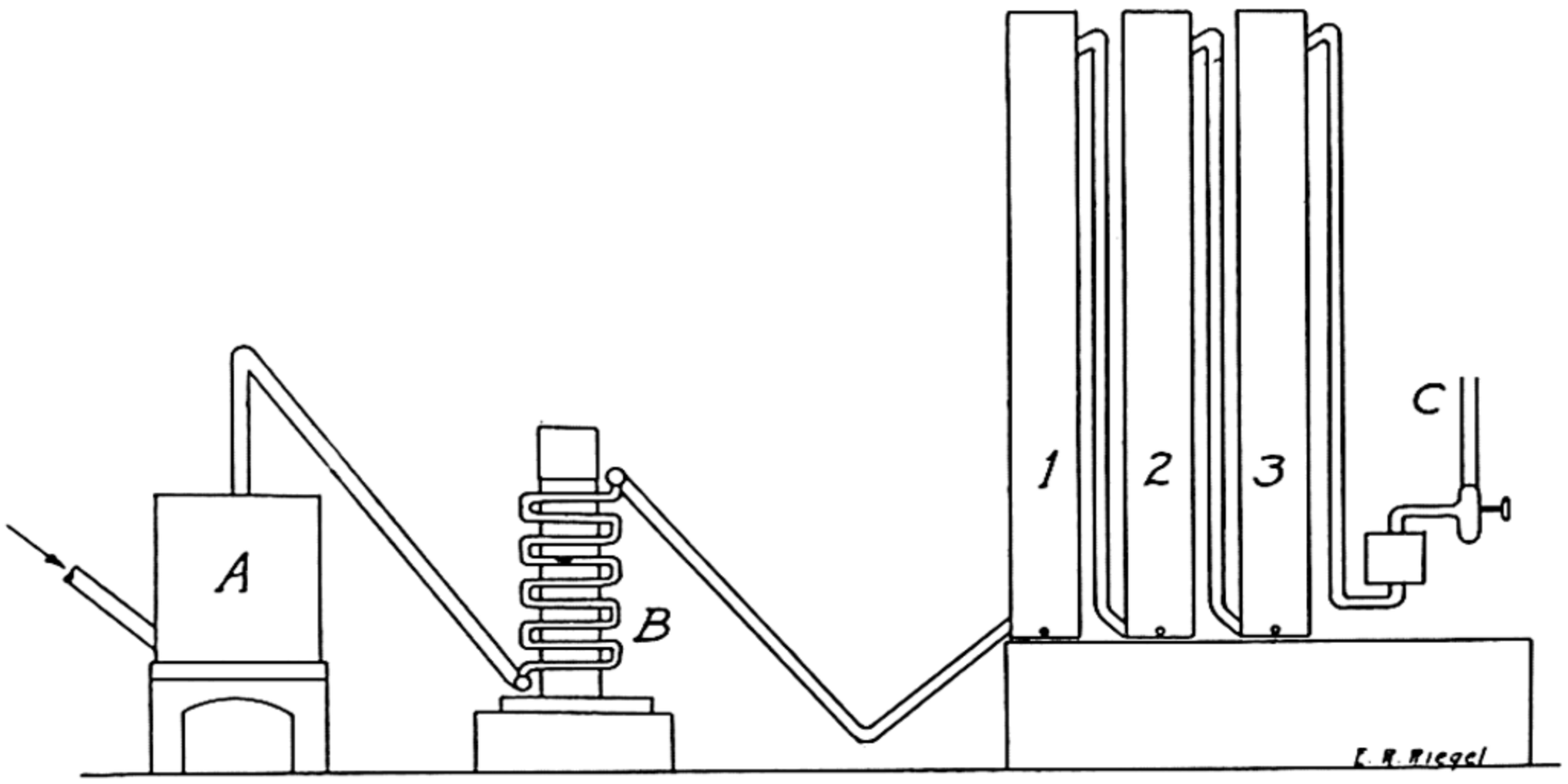


FIGURE 28.—Absorption system for hydrochloric acid; the gas enters dry box *A*, then cooler *B*, and the absorbing towers 1, 2, and 3; the exhausted gas passes out at *C*.

consequent necessity of scrubbing the gas to be reworked, by using the undiluted gases in a system closed as to escape gases.

Acid made by method (1) has a pale yellow color; it is shipped in glass carboys of 12-gallon capacity, set in a wooden protecting box, or in rubber-lined wooden tanks, four tanks to a flat railroad car, or, to a lesser extent, in steel tanks lined with wood impregnated with a wax tar. The content of arsenic is usually 0.0002 per cent As_2O_3 in the commercial acid; this low figure is due to the use of contact sulfuric acid which is made from carefully purified sulfur dioxide gas, itself obtained from selected ore or from sulfur. For certain purposes a still purer acid must be furnished; from the pot stills, an acid is made with an arsenic content of 0.00005 per cent As_2O_3.

The production of hydrochloric acid expressed as 100 per cent HCl in 1946 was 341,580 short tons. The 20° Bé. acid was quoted at $35.00 a ton; the 22° Bé. acid at $45.00 a ton. The relative production by the several methods differs from year to year. At one time, 67 per cent of the total for

[21] "High-boiling solvents from natural gas pentanes," Lee H. Clark, *Ind. Eng. Chem.*, 22, 439 (1930), with 2 flow-sheets.

[22] U. S. Patent 1,414,762; *see also* N. A. Laury, "Hydrochloric acid and sodium sulfate," Chapter 8. New York, Reinhold Publishing Corp., 1927.

the year came from the salt-cake furnace, and 33 per cent from chlorine, or as a by-product. There is an interesting relation between the several products involved. In making synthetic HCl, the sodium in the salt is obtained as caustic soda, while by the furnace method, it appears as salt cake. Depending upon market conditions, it may be more desirable to operate in one way instead of the other.

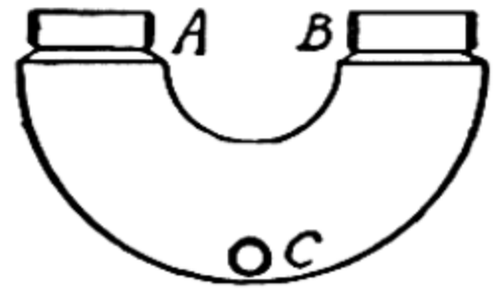


FIGURE 29.—Cellarius stoneware vessel for gas cooling; the gas enters at *A* and leaves at *B*; the vessel is set in running water, with only the bells protruding. *C* is the outlet for any liquid which may condense.

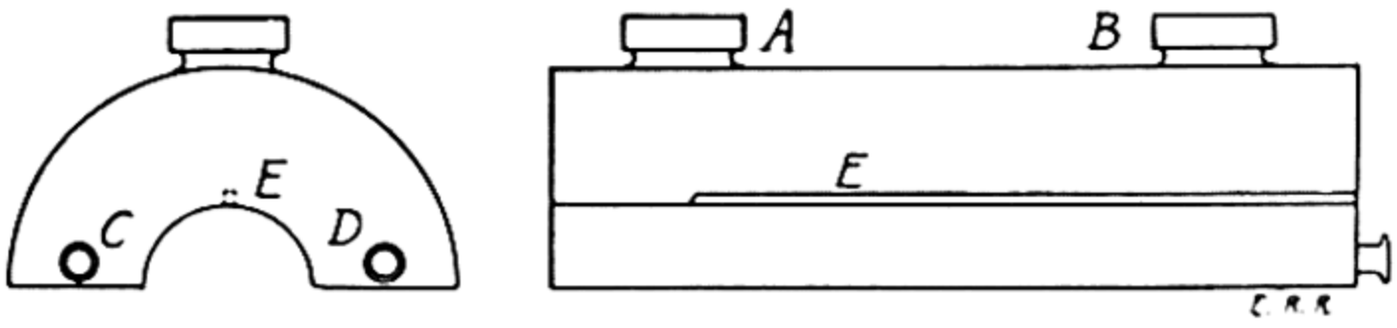
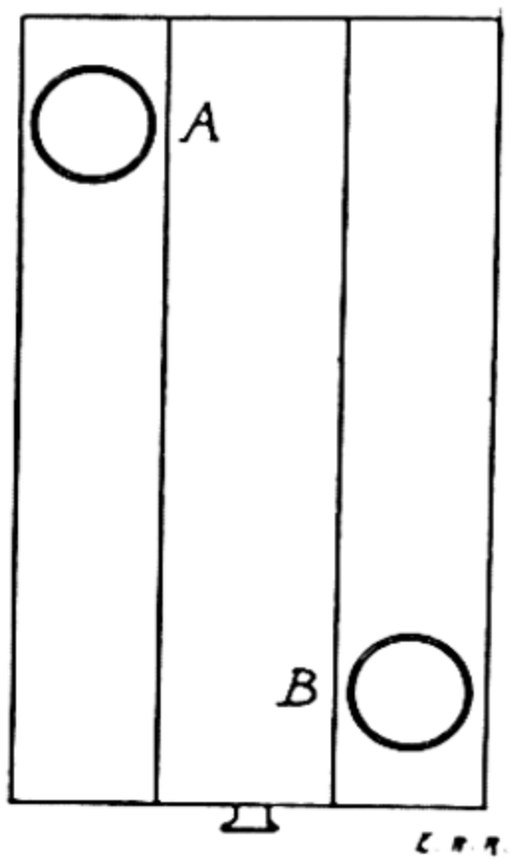


FIGURE 30.—Cellarius stoneware vessel for acid cooling and absorption; the gas enters at *A* and leaves at *B*; the acid solution enters at *C* and must travel to the rear of the vessel and then forward again in order to reach the outlet *D*, because dam *E* is in the way. The vessel is submerged in water.



Hydrochloric acid is used to clean steel before galvanizing (dipping in melted zinc), in wire steel plants, in the manufacture of dyes, of phenol, and for a number of minor purposes.

GLAUBER SALT

Glauber Salt ($Na_2SO_4 \cdot 10H_2O$) is a purified salt cake; the Glauber plant is usually adjacent to the salt cake storage bin.

Salt cake is dissolved in hot water, preferably in a circular wooden tank with stirrer. Steam is passed in during the solution to make up for cooling to the air. The solution is made as strong as possible (32° Bé. hot), lime is added to neutralize the sulfuric acid invariably present, and to precipitate iron hydroxide and alumina. The liquor is allowed to settle, and the clear portion is run into the crystallizers. The muddy bottom is filter-pressed, and the filtrate sent to the crystallizers.

The latter are usually wooden forms lined with lead, 15 feet long, 6 feet wide, and 2 feet deep. On standing over night, crystals form; the mother liquor is then run off by removing a wooden plug from the outlet in the bottom of the crystallizer, and the crystals are shoveled into low trucks on wheels; these are pushed to one of several openings in the floor, through which the crystals are dumped into the storage bin and shipping room below. The mother liquor is collected in a low tank and pumped into the dissolver, replacing, after being heated, a part of the water.

The crop of crystals in the winter months is greater than in the summer; in fact during hot spells it may happen that no crystals at all form. For this reason, a stock of crystals is accumulated in the winter and spring, and stored in bins closed on all sides. Ventilation must be avoided, for Glauber Salt loses its water of crystallization on exposure to the air.

Glauber Salt is crystallized from an acid liquor to obtain colorless crystals; from a neutral liquor, slightly colored brown crystals form. The composition is:

	Per Cent
Na_2SO_4, $10H_2O$	97.52
NaCl	.21
Moisture	2.23
$Fe_2(SO_4)_3$	.01
$CaSo_4$	.022
Free acid	.008

In a few plants, iron crystallizers are used, and the liquor is kept alkaline; this results in a product slightly off color.

Glauber Salt is used extensively in the textile industry; in 1946, 167,153 tons were produced; the market price, averaged between high and low, was $25.00 a ton. Its manufacture is interesting not only because of the high purity obtained but because, by making the first hot solution strong enough, no concentration of any kind is needed. This principle is followed in the chemical industries whenever possible.

Sodium Silicate

Sodium silicate is made by fusing together sand and soda ash in the proportions of 100 pounds of sand to 52 pounds of soda ash. Its formula is somewhat indefinite; it lies between $Na_2O \cdot 3SiO_2$ and $Na_2O \cdot 4SiO_2$. It occurs chiefly as a thick syrup, a water solution of the solid (30° to 40° Bé.). Sodium silicate is commonly called "water glass," because when solid it actually is a glass, and because this glass, unlike lime-soda glass (ordinary window glass) is soluble in water. The melting is performed in large tank furnaces similar to the window-glass furnace.[23] The materials are introduced in batches, at intervals; the product may be drawn off continuously or periodically. A mixture of sodium sulfate and coal may be used instead of part of the soda ash.

As the melt leaves the furnace, a stream of cold water shatters it to fragments; these are dissolved by means of superheated steam in tall, rather narrow steel cylinders with false bottoms,[24] and the resulting liquor clarified.[25] Sodium silicates are sold in solutions which vary from the most viscous, 69° Bé., to thinner ones, reaching finally 22° Bé. solutions, adapted for paints. The dry material in the form of a powder is also on the market, and is made by forcing the thick liquor through a very fine opening into a chamber swept by a rapid current of cold air, which carries off the moisture.[26] Because sodium silicate is hygroscopic, powdered sodium sulfate is sometimes incorporated with the solid silicate[27] to prevent caking. In

[23] Chapter 11. [24] U. S. Patent 1,385,595. [25] U. S. Patent 1,132,640.
[26] German Patent 249,222. [27] U. S. Patent 1,139,741.

composition, the sodium silicates may be varied from 1 $Na_2O \cdot 2/3\ SiO_2$, to 1 $Na_2O \cdot 3.9\ SiO_2$; they differ in alkalinity from pH 13.2 for $Na_2O \cdot 2/3\ SiO_2$, to pH 10.8 for the $Na_2O \cdot 3.9\ SiO_2$ silicate, measured in 1 per cent solutions. In the concentrated solutions, the pH is not very different. Each of the commercial ratios results in a liquid with special properties, rendering it the proper selection for a specific purpose.[28]

The uses of sodium silicate are surprisingly numerous; it is added in the crutching of soap;[29] it serves to impregnate wood, to weight silk, as a mordant, as a heat-resistant binding agent, to clarify juices and solutions, to render bricks and cements non-porous, as a detergent, and as an adhesive, particularly in making corrugated paper boxes. The 1946 production was 412,357 tons (on the anhydrous basis). Sodium silicate as 40° Bé. solution, (drums) carload lots, was $16 a ton in 1946.

Bromine and Bromides

When the brines from which table and dairy salt is made contain bromides, the bromine may be recovered from the mother liquors. The oldest process, still in use, is to concentrate the mother liquor and to treat it in a stone still (untarred) with sulfuric acid and sodium chlorate (formerly with manganese dioxide); a current of steam carries off the bromine liberated. An earthenware coil receives the mixed steam and bromine and condenses both, by water cooling; two layers collect in the stoneware receiver; the lower one is the dark red, liquid bromine; the upper one, bromine water. They are separated, and the bromine, from the water layer may be recovered by blowing with air or natural gas. This lean bromine gas is treated separately; it is passed through a small stoneware tower filled with moist iron filings, and a strong solution of ferric bromide forms, from which the bromine is displaced by chlorine gas. Bromine is a liquid which boils at 63° C. (145° F.)

In another process the brine is treated directly with chlorine gas; still another process is based on the fact that on electrolyzing a bromide-bearing brine, the bromine is liberated first, the chlorine only later.

Crude bromine is purified from chlorine, its chief impurity, by a redistillation, passing the vapor over iron filings which retain the chlorine.[30]

Bromides are made by saturating caustic soda (for sodium bromide, NaBr) with bromine; a smaller amount of sodium bromate is simultaneously formed,

$$6NaOH + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O.$$

Bromides are valuable pharmaceuticals; bromine serves in the manufacture

[28] Several interesting and instructive bulletins on this subject may be obtained by addressing the Philadelphia Quartz Company, Philadelphia, Pa. See also "Sodium metasilicate as an industrial alkali," James C. Vail, *Trans. Am. Inst. Chem. Eng.*, 25, 123 (1930).

[29] Chapter 32.

[30] A list of patents relating to these various processes will be found on page 93, *Dept. Interior Bull.* **No. 146**; *see* reading references; the first two patents were U. S. Patents No. 460,370 (1891) and No. 11,232 (reissue 1892).

of certain dyes[31] as a disinfectant; its irritating and suffocating properties have led to its use as a war gas.[32]

At Wilmington, N. C., bromine is obtained from sea water,[33] which contains 0.0064 per cent (average) of bromine; 1800 gallons of sea water must be treated for each pound of bromine obtained. This plant is now the largest American producer. A second plant using sea water as source is the Freeport, Texas plant of the Dow Chemical Company, also a large producer. Bromine is obtained also at Midland and Saginaw, Michigan, in Ohio, and in West Virginia. A large part of the world's supply formerly came from Stassfurt, Germany. A salt deposit rich in bromides and readily flooded by controlled amounts of sea water occurs in Tunis.[34]

Bromine and bromine in compounds sold or used by producers in the United States during 1945 came to 79,709,857 pounds which represents a drop of 22 per cent from the all-time high of 102,112,462 pounds in 1944.[35] The price for bromine in 1945 varied from 21 to 30 cents a pound. The production figure is three times that for 1936.

The use of ethylene bromide with tetraethyl lead as an antiknock compound[36] in gasoline engines has meant a large consumption, supplied first by imports, but more and more, by domestic producers. The increasing production of bromine has made this possible.

Other Patents

U. S. Patent 1,165,815 (1916) to Thelen and Wolf, on a mechanically operated salt-cake furnace; German Patent 325,314, on preheating the charge for the Mannheim furnace; German Patent 295,073, to Henry Howard, of Massachusetts, on serving salt and sulfuric acid direct to Mannheim furnace. U. S. Patent 1,907,987, soda ash; 1,940,459, manufacturing soda ash; 2,035,441, apparatus for manufacture of sodium carbonate monohydrate; 2,038,025, sodium sesquicarbonate from bicarbonate; 1,928,540, manufacture of sodium bicarbonate; 1,921,505, low apparent density sodium carbonate; 1,868,949, sodium sulfate production; English Patent 375,039, electric heat for the salt-sulfuric acid reaction; Can. Patent 396,040; U. S. Patent 2,242,507, to make sodium sulfate and ammonium chloride; 2,208,175, production of sodium sulfate. German Patent 489,917 and 516,348, mechanical salt cake furnace; U. S. Patent 1,853,330, distillation and concentration of hydrochloric acid; German Patent 558,553, same, with the aid of added $CaCl_2$; German Patent 535,355, same, and recovery of acetic acid and HCl from the same vapors; 1,902,801, continuous process of preparing liquid bromine; 1,917,762, extracting bromine from dilute solutions; 1,930,143, bromine recovery from spent developers; 1,919,721, preparation of bromates; Brit. Patent 523,607 (1940), on bromine from sea water; Russ. Patent 54,404 (1939); U. S. Patent 2,245,514, and 2,251,353, all three concerning bromine.

Problems

1. (a) A plant intends to manufacture 300 tons of Solvay ammonia soda per day; the soda to be 98.8 per cent Na_2CO_3. How much salt will be required per day, if its NaCl content is 99 per cent, for the actual conversion? How much salt is required since the carbonating towers consume 66 per cent of the salt, the rest being wasted?

[31] Thus eosine, Chapter 28.
[32] Chapter 34.
[33] "Commercial extraction of bromine from sea-water," Leroy C. Stewart, *Ind. Eng. Chem.*, 26, 361-369 (1934), with 20 illustrations.
[34] "The future demand for bromine," C. R. De Long, *Ind. Eng. Chem.*, 18, 425 (1926).
[35] "Minerals Yearbook," 1945.
[36] Chapter 24.

At what point or points is the salt lost which is not used? (b) What is the weight of the bicarbonate of soda made as intermediate product?

2. The ammonia NH_3 which takes part in the reaction is about one-third the weight of the soda ash produced. For the production of the soda ash specified in Problem 1, how much carbon dioxide is needed for the actual final product, and how much limestone, 95 per cent $CaCO_3$, must be calcined in order to obtain it? Is the lime obtained simultaneously sufficient for the regeneration of the fixed ammonia, or is it an excess, or is there a deficiency? (Leave fire gases in kiln out of consideration.)

3. Referring to Problems 1 and 2, let there be once again the amount of ammonia in process as found to have reacted, mainly in the absorbers, and some in the tower liquor and filtrate from the bicarbonate. How much would the ammonia be worth (at 5 cents a pound NH_3), compared to the value of the soda ash produced? The amount of carbon dioxide in process is again as much as leaves the plant in the soda ash, mainly returned from the calciner. How much calcium chloride in solution form leaves the ammonia still, in its run-off?

4. A plant manufactures soda of 99.5 per cent purity. The amount of salt actually transformed in the operation is 37 tons. The reaction $NH_4HCO_3+NaCl \rightarrow NaHCO_3+NH_4Cl$ takes place to the extent of 75 per cent. How much salt is taken originally, how much left unused; what is the tonnage of soda ash made, if the calcination is performed without loss? What is the weight of bicarbonate of sodium, expressed as dry $NaHCO_3$?

5. In a Mannheim furnace, there are charged per day 6500 pounds of salt mixed with a certain amount of nitre cake. If the nitre cake has the theoretical composition for $NaSO_4$, how many pounds of the latter must be charged per hour? Assuming the recovery of salt cake to be 98 per cent, how many tons of salt cake will be collected per day?

6. From the salt charged as described in Problem 5, hydrochloric acid is recovered with an efficiency of 89 per cent; it is made into 31 per cent HCl (about 20° Bé.). How many pounds of acid will be collected per day?

7. 4100 pounds of 96.5 per cent salt cake is made into Glauber salt, which has the analysis shown in the text. How many pounds of Glauber salt will be obtained, assuming that the mother liquors are worked up constantly so that the yield is 94 per cent? What will be the factor, salt cake to Glauber salt? (1 lb. salt cake produces x lbs. Glauber salt.)

8. It is desired to prepare 9 tons of sodium silicate syrupy, to test 38.8° Bé. The composition of the dissolved silicate is to correspond to $Na_2O \cdot 3.36SiO_2$. The specific gravity given corresponds to 36 per cent of the 3.36 silicate. How much soda ash 99 per cent, and how much sand 100 per cent will be required, the yield being assumed to be 92 per cent?

9. A brine is saturated and contains on analysis NaCl 298 grams per liter; $CaSO_4$ 5.1 g.p.l.; $CaCl_2$ .81 g.p.l.; $CaCO_3$ .15 g.p.l.; $MgCl_2$ .48 g.p.l. The non-NaCl materials restrict the amount of NaCl which the equal brine would hold at saturation. If that amount of salt is proportional to the equivalent of the foreign salts, what is the amount of NaCl which the brine will hold at saturation?

10. The crude Solvay $NaHCO_3$ crystals always contain ammonium in the ratio of $5NH_4$ to 95 Na, and it cannot be washed out; it is assumed that a double salt forms. It is only on calcining that the ammonia is liberated. NaCl and Na_2SO_4 on the other hand wash out readily at the filter. For the weight of bicarbonate in Problem 1 (b), and in Problem 4, how much ammonia does that represent per day? In what way is it saved to the system?

Reading References

"The manufacture of soda," T. P. Hou, 2nd ed., New York, Reinhold Publishing Corp., 1942.

"Salt-making on the great Salt Lake," Thomas B. Brighton, *J. Chem. Educ.*, 9, 407 (1932).

"Vast raw material resources await chemical development," W. M. Weigel, *Chem. Met. Eng.*, 39, 366 (1932). Salt, sulfur.

"Milling salt in Texas," H. B. Cooley, *Chem. Met. Eng.*, 39, 390 (1932).

"Salt domes in Louisiana and Texas," R. A. Steinmayer, *Chem. Met. Eng.*, 39, 388 (1932); the same article with detailed maps and 8 drawings in *Am. Inst. Chem. Eng., Trans.*, 25, 239 (1930).

"The value of silicate of soda as a detergent—II," John D. Carter, *Ind. Eng., Chem.*, 23, 1389 (1931).

"Technology of salt making in the United States," W. C. Phalen, *Bur. Mines Bull.* No. 146, (1917).

"The salt and alkali industry," Geoffrey Martin, London, Crosby, Lockwood and Son, New York, D. Appleton and Co., 1916.

"Hydrochloric acid and sodium sulfate," N. A. Laury, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1927.

"Hydrochloric acid and salt cake," Vol. V of Lunge Series on the "Manufacture of Acids and Alkalis," A. C. Cumming, London, Guerney and Jackson; 1923; New York, D. Van Nostrand Co.

"Alkali lakes brines supply western soda producers," W. Hirschkind, *Chem. Met. Eng.*, 38, 657 (1931).

"California desert soda," G. Ross Robertson, *Ind. Eng. Chem.*, 23, 478 (1931).

"Salt, a by-product of condenser cooling," Otto M. Smith, *Ind. Eng. Chem.*, 24, 547 (1932).

"Is there a profit in chlorine and nitrate from salt?" F. W. DeJahn, *Chem. Met. Eng.*, 42, 537 (1935).

"Commercial extraction of bromine from sea water," Leroy C. Stewart, *Ind. Eng. Chem.*, 26, 361 (1934), with 20 illustrations.

"The culture of certain silicate gardens," James G. Vail, *Ind. Eng. Chem.*, 26, 113 (1934).

"Glauber salt in North Dakota," Irvin Lavine, Herman Feinstein and Earl Skene, *Chem. Met. Eng.*, 42, 681 (1935).

"Die Sodafabrikation nach dem Solvay-Verfahren," Julius Kirchner, Leipzig, S. Hirzel, 1930.

"Development of 'Karbate' materials and their applications," M. R. Hatfield and C. E. Ford, *Trans. Am. Inst. Chem. Eng.*, 42, 121 (1946).

"Synthetic hydrogen chloride," Aylmer H. Maude, *Chem. Eng. Progress*, 44, 179 (1948).

"Absorption and purification of hydrogen chloride from chlorination of hydrocarbons," C. F. Oldershaw, L. Simenson, T. Brown and F. Radcliffe, *Chem. Eng. Progress*, 43, 371 (1947).

"Bromine," *Industrial Chemist*, 22, 577 (1946).

Wherever possible, the salts of sodium are used in preference to those of other metals, for the salts of sodium are soluble and cheap. The cheapness is due to the abundance of common salt, NaCl, the source (as to metal) of nearly all other sodium salts.

Chapter 4

Sodium Sulfide, Sodium Thiosulfate (Hypo), Anhydrous Bisulfite of Sodium, Sodium Hyposulfite

In a modern chemical establishment manufacturing a number of heavy chemicals for the general trade, there is a relation between the various sections, in that the product of one becomes the raw material for the next. Sulfuric acid, the first product, is the only exception; it is made entirely from purchased materials (sulfur or pyrite), or from by-product sulfur dioxide gas from a smelter. The preparation of nitric acid from sulfuric acid and sodium nitrate in retorts is accompanied by the production of nitre cake, and this must be supplemented, when necessary, by its manufacture from salt and acid in the pot stills; the nitre cake fused with salt gives hydrochloric acid and salt cake (Na_2SO_4). A large amount of salt cake is sold as such; the remainder is heated with coal or coke and made into sodium sulfide, Na_2S. By-products of this are sodium carbonate, Na_2CO_3, and sodium sulfite, Na_2SO_3, which are properly worked up into sodium thiosulfate, $Na_2S_2O_3$, usually called "hypo" from its old name of hyposulfite, now abandoned. Not all sodium sulfide is made from salt cake, for although the latter is the cheapest raw material, furnaces, leaching tanks, and other equipment are required; for small-scale operations, soda ash and sulfur are more suitable. In large plants, such as the one described above, caustic soda, chlorine, and soda ash are not usually included, but all those products which require sulfuric acid for their manufacture [1] are part of the plant. Soda ash is usually purchased in considerable quantities, for it serves to make anhydrous bisulfite of soda, $NaHSO_3$, sodium hyposulfite (hydrosulfite), $Na_2S_2O_4$, and, following the older process, sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$; plants for these three products properly belong to an establishment which includes the manufacture of sulfuric acid, because the sulfur dioxide required may be taken from the burner house by simply erecting a pipe line. To complete the description, a power house for steam and electric current generation would be included; also water pumps for cooling, washing, and absorbing water; shipping facilities, and offices.

A modification of the set-up outlined will make good the lack of nitre cake, and sodium sulfate from nitre cake, by purchasing natural sodium sulfate. The nitric acid would then also have to be purchased from synthetic ammonia plants, or the ammonia might be purchased, and the oxidation performed in the old nitric plant, remodeled for the purpose.

[1] Chapter 2; but not superphosphate (Chapter 7), which is a specialty.

Sodium Sulfide

Sodium sulfide, Na_2S, has become extremely important as a depilatory,[2] in the manufacture of sulfur dyes, and, in solution, as a solvent for the same sulfur dyes.[3] It was formerly produced altogether in the form of crystals, $Na_2S \cdot 9H_2O$, which in the commercial form contained about 30 per cent Na_2S; the crystals are brown, whereas pure sodium sulfide crystals are colorless. These crystals are still made, but the greater part of the sulfide is now marketed in the form of concentrated sodium sulfide with 60 per cent Na_2S, as solid cakes and lumps, or as flakes ("chips"). The method may be outlined as follows: Salt cake (or roast cake) from the Mannheim furnace mixed with coal is heated in a reverberatory furnace; a melt is produced which is raked out and either dissolved in water at once, or allowed to cool to solid cakes which are later leached with hot water. The solution is made strong enough so that when it is cooled in shallow pans, crystals of $Na_2S \cdot 9H_2O$ form. To produce the 60 per cent sulfide, the crystals are melted in special pots and water driven off from the hot liquid; on cooling, a black solid with red fracture forms. Another method is to boil down the first solution after filtering or settling, until the sodium sulfide content is a little above 60 per cent.

Reverberatory Furnace. A reverberatory furnace is shown in Figure 31; it is a low arch furnace with a fireplace separated from the hearth by a bridge wall. The fire gases strike the roof over the fireplace and are deflected onto the charge on the hearth; the low arch forces intimate contact between fire gases and charge. From the furnace proper the gases pass to the preheating chamber, of dimensions similar to those of the hearth, and from there to the stack. For a furnace whose hearth is 12 feet long and 8 feet wide, the charge is 1000 pounds of salt cake [4] and 500 pounds of coal screenings. Such a charge is shoveled into the rear of preheating chamber, where it is warmed by the outgoing gases for an hour. It is then pushed with a hoe to the working hearth and heated there, with occasional stirring, for another hour, when it is ready to be pulled out. Instead of shoveling in the charge, it may be fed in from an overhead bin through an opening in the arch. Melted sulfide is extremely corrosive, so that the construction of the furnace is a special one. The floor of the hearth consists of alunite or other basic bricks, set upright on their smallest face. These bricks rest on several thicknesses of asbestos paper soaked in silicate of soda solution; such an underlining has been found efficient in preventing the escape of melt. The alunite bricks are placed in a solution of silicate of soda for some hours just before laying. The hearth side of the bridge wall is also lined with alunite bricks, while the fireplace side and the arch over the whole furnace are of ordinary fire bricks. The rear wall is usually lined with a hard firebrick. Such a furnace will last 8 to 12 months, when it must be rebuilt.

[2] Chapter 36.
[3] Chapter 28.
[4] Instead of salt cake, nitre cake was formerly used; the escaping sulfuric acid caused a cloud at the top of the stack, which caused much difficulty with municipalities. It was thought that by substituting salt cake, the cloud would vanish; but to everybody's surprise, it continued. In this case, it is due to sublimed sodium salts; these may be removed from the stack gases by a Cottrell precipitator; *see* Chapter 43.

In order to insure a high yield the atmosphere in the furnace must be a reducing one; the fire gases should contain one or several per cent carbon monoxide and no oxygen. Such fire gases are obtained by building a deep bed of coal on a fireplace of rather small dimensions, using soft coal and forced draft. The reactions on the hearth are:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$
$$Na_2SO_4 + 4CO \rightarrow Na_2S + 4CO_2.$$

There are several ways in which the melt may be handled on leaving the furnace. A simple and efficient way is to pull the charge into 8 or 10 buggies on wheels, each holding 80 to 100 pounds, so that one man can handle them. Another way is to pull the charge into two steel boxes on low trucks.

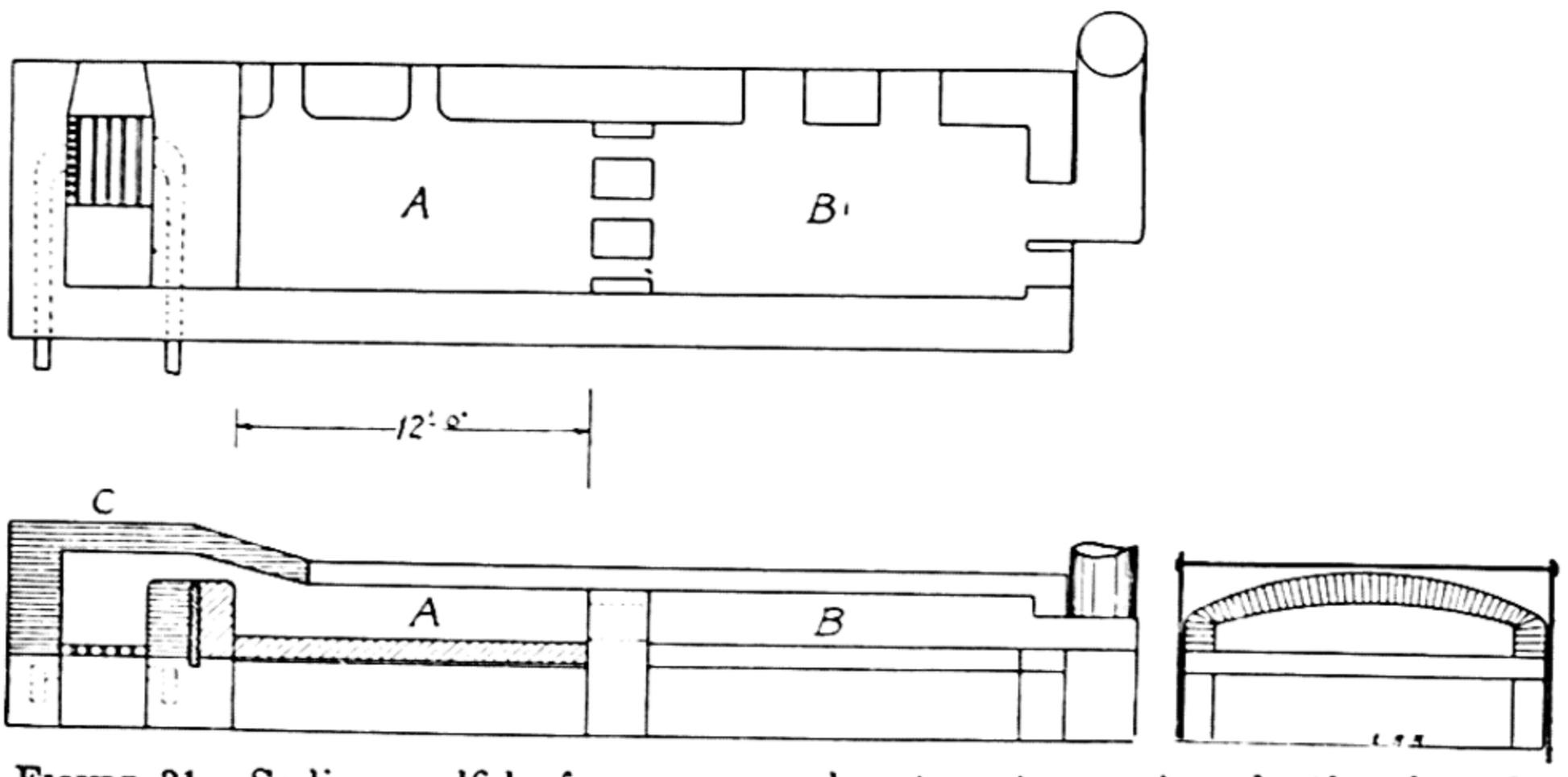


FIGURE 31.—Sodium sulfide furnace, reverberatory type; *A*, reduction hearth; *B*, preheating chamber. The fireplace and half of the bridge wall are of hard firebricks; *C*, the hearth of alunite or aluminate bricks.

In either case the melt is allowed to cool; during the cooling of the cakes, some further reduction takes place. The cold cake is broken with a sledge and fed to an edge runner [5] washed by a constant flow of warm water. A solution of sodium sulfide with suspended matter results, which is elevated to a settling tank. In the older plants, the cake is fed to a jaw crusher [5] in the floor, then elevated to one of four leaching tanks which are worked in series; each tank accommodates one day's melt. The fresh melt is wetted with the wash from the melt of the day before, and this wash in turn has first rested on the nearly spent melt of two days before; the fourth tank is being emptied. In this way each melt is leached three times.

A totally different way is to pull the melt into a ladle and to bring it over a dissolving tank with a stirrer. The fluid melt, still hot, is run into the water, which is thereby heated; this operation is extremely noisy. It utilizes a part of the heat of the melt, however, and saves labor, so that it will probably become standard, at least for large plants. The suspension may be settled or filter-pressed using iron wire filter cloth; the press cake is made

[5] Chapter 44.

up with water once more, filter-pressed again, and the filtrate used in the dissolving tank.

The melt in the cakes is 60 to 65 per cent Na_2S; such rich melts flow less easily than melts contaminated with unreduced sulfate or with carbonate

The sulfide liquor obtained by any of these variations is hot, and of such strength that after it is run into shallow iron pans, crystals deposit over night. The mother liquor contains sulfide, and also sulfate, sulfite, and carbonate; it may be concentrated, when all the salts other than sulfide precipitate, leaving a concentrated solution of sulfide which may usually be crystallized; in some cases it may contain so much silicate that it will not crystallize. The precipitated salts are dissolved in water and the solution used for making thiosulfate. The brown crystals with 30 per cent Na_2S may be sold as such, or they may be placed in iron pots over a fire, melted, and enough water removed to raise the content of Na_2S to 60 per cent. The liquor may be run into concentrating pans directly and evaporated to the higher strength; the difficulty in that case is that the sulfate, carbonate, and similar impurities deposit during the concentration and coat the bottom of the concentrating pans, causing them to become locally overheated, which results in leaks.

The 60 per cent liquor may be run into shallow flat pans, where it solidifies over night; it is then broken and shipped as lumps. There are many other ways to fix the final shape of the product; the best one is to feed a thin layer to a water-cooled rotating drum, actuated by a ratchet; a knife detaches the cake, and the thin strips fall and break into still smaller flakes, called chip sulfide.[6] In this form, solution at the consumer's plant is greatly facilitated. The color of chip sulfide is red; like any other form of sulfide it must be stored in air-tight, thin, steel drums; otherwise it turns green because of the formation of sulfate and carbonate.

New Types of Sulfide Furnaces. The old reverberatory furnace is a reliable way to manufacture sulfide, but new types of furnaces are displacing it. The aim of the newer furnaces is to reduce labor to a minimum by a continuous operation, largely automatic. On one of these furnaces, a rotary style[7] is proposed with carbon monoxide gas, prepared in auxiliary vessels, as reducing agent and fuel. Several German proposals are promising also; one[8] involves the use of a Bessemer pear such as is used for making steel, and still another[9] proposes ovens with pendulum or shaking motion. Two blast furnaces have been patented; one proposal[10] allows the melt to solidify; in the other[11] the fluid melt is either tapped at intervals or drawn off continuously. In the latter furnace, as well as in one proposed by H. K. Moore,[12] the fluid melt is dropped at once into a "quench tank." Finally, studies in the application of the electric furnace to the manufacture of sodium sulfide have been made[13] and were applied commercially in Italy during the war of 1914-18.

The annual production of 60 to 62 per cent sodium sulfide, also called

[6] U. S. Patent 915,633.
[7] U. S. Patent 1,397,497.
[8] German Patent 388,545.
[9] German Patent 389,238.
[10] German Patent 255,029.
[11] German Patent 273,878.
[12] U. S. Patent 1,130,317.
[13] *Chem. Abstracts,* 15, 3423 (1921).

"solid sulfide," is approximately 40,000 tons. The price in 1946 varied between $63 and $78 a ton. The crystals (30 per cent Na_2S) are sold in 440-pound drums, at $48 a ton.

In 1942, there was developed at Höchst (Germany) a method of producing sodium sulfide (62 per cent Na_2S) directly from sodium polysulfide, by the action of the latter on sodium amalgam:

$$Na_2S_4 + 6Na \rightarrow 4Na_2S.$$[14]

The amalgam is produced in the mercury caustic cell; the polysulfide is introduced into the decomposing chamber of the mercury cell. It is necessary to maintain the temperature of the decomposing chamber at 90° C. (194° F.).

Sodium Thiosulfate

Sodium thiosulfate,[15] $Na_2S_2O_3 \cdot 5H_2O$ or "hypo," is the agent employed in photography for dissolving the unreduced silver salts, and in textile mills as an "antichlor." It is made in two ways: the first is independent of any other process, and requires soda ash and brimstone; the second makes use of by-product sulfide liquors and is dependent upon a sulfide plant; its sulfur dioxide may be drawn from the burner house of the sulfuric acid plant generally forming part of a large establishment. It is customary in the second kind of plant to have in reserve soda ash and brimstone, so that in case the by-product liquor fails, these materials may be used instead. The same apparatus serves without any change, and burner gas is the source of sulfur dioxide, as before.

The Soda Ash-Brimstone Process. Soda ash is dissolved in hot water and the solution (26° Bé.) pumped to a small storage tank at the top of the first of two absorption towers. These are of lead supported on wooden beams, and are filled with hardwood sticks, except in the lower part where a small chamber of hard acid bricks is provided. The nearly spent sulfur gas from the second tower (second with respect to the liquor) enters at the base and meets the descending soda ash solution which absorbs all the remaining sulfur dioxide. The partly gassed liquor from the first tower is elevated to the top of the second tower wherein it meets the sulfur dioxide gas fresh from the burners; the soda ash is completely changed to sodium bisulfite, which runs out through a seal at the base of the tower and is collected in lead-lined receiving tanks.

$$Na_2CO_3 + H_2O + 2SO_2 \rightarrow 2NaHSO_3 + CO_2.$$

Figure 32 indicates the dimensions and disposition of the apparatus. The nitrogen, oxygen, and carbon dioxide pass out of the first tower to a small stack.

Sulfur dioxide may be made by burning brimstone in iron pans cooled from below by air, and set in brick work; or, a special patent burner may be installed, such as the Glens Falls (N. Y.) rotary burner, the Chemico spray burner (Chapter 1), the Vesuvius burner with shelves, and others.

[14] P. B. number 30374. See also *Chem. Industries*, 61, 49 (1947).

[15] An old name for the same substance is sodium hyposulfite, from which the name "hypo" originated.

Formerly the bisulfite liquor, with 22 per cent SO_2 content, was an important product; it has been replaced by anhydrous bisulfite of soda, a powder with 60 per cent SO_2, described later. By means of soda ash, the bisulfite liquor is changed into neutral sulfite, and this is heated with powdered brimstone[16] in a brick-lined, cast-iron vessel with a stirrer. A solution of sodium thiosulfate results; it is concentrated hot in a boiler from 36° Bé. to 51° Bé. After settling, this liquor is run into lead-lined or steel

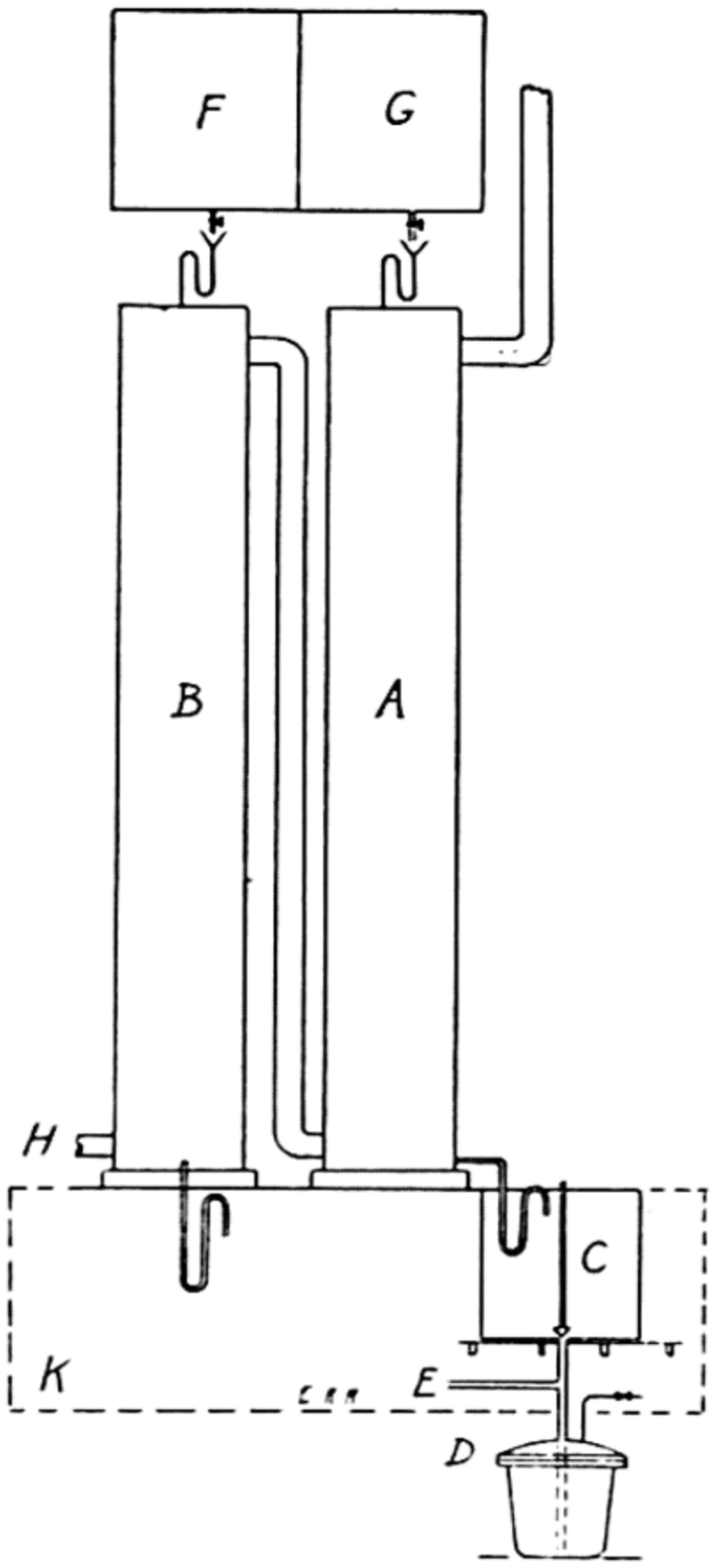


FIGURE 32.—A simple plant showing the working principles for making sodium bisulfite solution. Soda ash solution in tank *G* is fed to the first lead tower, *A*, where it meets the weak gas from the top of the second lead tower, *B*. The liquor from *A* collects in *C*, is run into the lead-lined cast-iron pot *D*, used as a blowcase, and forced through *E* to tank *F*, from which it is fed to tower *B*, meeting fresh gas entering at *H*. The finished liquor collects in the storage tank *K*. The towers are packed with wooden grids.

crystallizers and allowed to cool. When iron crystallizers are used, a crust of the crystals is left on the sides and bottom to avoid contamination.

$$2NaHSO_3 + Na_2CO_3 \rightarrow 2Na_2SO_3 + H_2O + CO_2$$
$$Na_2SO_3 + S \rightarrow Na_2S_2O_3.$$

After two or more days, the mother liquor is run off, the crystals $Na_2S_2O_3 \cdot 5H_2O$ are shoveled to centrifugals which remove adhering mother liquor, washed by a short spraying from a hose, and dumped to a conveyor leading to the interior of a rotating cylindrical steel wire screen. The screen consists of two sizes, a six-mesh half which receives the unassorted crystals, and a three-mesh screen which forms the rear half.[17] The fines drop through the

[16] The crushing of brimstone is not without danger.
[17] Compare Chapter 44.

six-mesh wire as the screen slowly rotates; the pea size drops through the three-mesh wire, while the coarser pieces, the "crystal" size, roll off at the far end of the wire. No drying of the crystals is necessary.

A fine crystal product of uniform size called "granulated hypo" is made by cooling the 51° Bé. liquor in circular steel pans 10 feet in diameter and 3 feet deep, in which a two-armed scraper slowly revolves while the liquor cools.

Sodium thiosulfate crystals effloresce so readily in air that they must be packed at once in air-tight containers, cartons or paper-lined barrels.

The By-Product Sulfide Liquor Process. The carbonate and sulfite which separate from the sulfide liquor while it is in process of concentration are made up with water; the adhering sulfide is also dissolved. This liquor becomes the raw material for sodium thiosulfate manufacture. In the plants which filter the suspension from the "quench tanks," and make up the first mud with water again, then filter once more, this second filtrate becomes the raw material for hypo; the first filtrate is essentially sulfide. The most satisfactory relation of the carbonate and sulfide (the sulfide is usually very low) is about 8 per cent Na_2S and 6 per cent Na_2CO_3, when the reaction

$$2Na_2S + Na_2CO_3 + 4SO_2 \rightarrow 3Na_2S_2O_3 + CO_2$$

takes place during the gassing period. An excess of sulfide over this amount must be avoided, as it may lead to a loss of useful materials in the generation of H_2S:

$$Na_2S + SO_2 + H_2O \rightarrow Na_2SO_3 + H_2S.$$

Some of this hydrogen sulfide will be changed into sulfur by sulfur dioxide, but it is manifestly cheaper to supply sulfur in the form of brimstone, if any is needed. Technical sodium sulfide always contains some polysulfides, and these supply some sulfur which reacts with such sulfite as may be present in the original liquor. Should the carbonate run high and the sulfur low, brimstone may be added to change the sulfite formed (the bisulfite is avoided [18]) into thiosulfate.

The sulfide-carbonate liquor may be treated with sulfur dioxide gas, the regular burner gas with 7 per cent SO_2, in towers. Instead of a single passage of the liquor through a rather tall tower, many passages through a shorter tower may be substituted; these are then called circulating towers. The liquor is run into a large tank and pumped at a rapid rate to the top of the tower, which has wooden shelves. As the liquor cascades from shelf to shelf, fresh surfaces are exposed and the absorbing liquid exhausts the gas readily. The gassed liquor at the base of the tower runs back into the original tank. The tower may be 20 feet high, 4 feet in diameter, of steel lined with bricks; the wooden shelves are perhaps 10 inches apart. Each shelf covers only about two-thirds of a circle, and the openings are staggered, so that the liquor changes direction constantly. Two or more towers may be used, the gas passing from one to the other to insure its exhaustion.

[18] Acidity due to $NaHSO_3$ is detected and measured by a titration with caustic in presence of phenolphthalein; Na_2SO_3 is neutral to phenolphthalein, but alkaline to methyl orange; it is measured, with any carbonate present, by a titration with standard acid, in the presence of methyl orange; $NaHSO_3$ is neutral to methyl orange.

After sufficient gassing, the liquor is filter-pressed through cotton duck cloth and concentrated in a steel boiler with a steam chest.[19] The crystallization and further steps are the same as described under the soda-ash brimstone process. It will be noted that in normal running the sulfide by-product liquor requires no brimstone addition.

In 1939, there were produced 25,714 tons of sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, valued at $44.50 a ton.

Anhydrous Sodium Bisulfite

The commercial methods[20] for manufacturing anhydrous bisulfite of sodium, $NaHSO_3$, a cream-colored crystalline powder, differ in detail, but are alike in general principle, namely, in passing 7 or 8 per cent sulfur dioxide into a suspension of soda ash in the mother liquor saturated with sodium bisulfite[21] from previous batches. When a new plant is started, a suspension of soda ash in a saturated soda ash solution may be used. There is produced a suspension of anhydrous bisulfite, which is passed through centrifugals. The wet powder remains; the mother liquor is collected in the "emulsion" tank and treated with soda ash to produce the suspension which is sent through the process again. The wet powder is dropped to a conveyor leading to a circular shelf drier with six shelves; rotating arms move the material from shelf to shelf, dropping it through alternate circumferential and central openings. The shelves are hollow steel, with steam circulation. The powder issues from the bottom warm and dry; a small inclined bucket conveyor lifts it into a hopper from which barrels are filled by pulling a slide.

By using a building with several stories, the material may be moved by gravity, except for feeding the soda ash to the emulsion tank, and lifting the soda ash emulsion to the absorbers. These operate in two stages; the first-stage absorbers, on the top floor, receive the soda ash emulsion and the sulfur dioxide gas which has already passed through the second-stage absorbers. The latter, on the floor below, receive the suspension from the first-stage absorbers by gravity, and the fresh sulfur dioxide gas from the sulfur or pyrite burners. Here the soda ash is completely transformed to anhydrous bisulfite, and this suspension is fed to the centrifugals on the floor below; the drier is on the ground floor, on a level with a railroad car floor.

The function of the drier is merely to remove adhering moisture; the anhydrous bisulfite is produced as such in the suspension.

$$Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2.^{22}$$

[19] Chapter 43.

[20] U. S. Patents 1,099,177; 1,084,436; 1,023,179.

[21] As soon as soda ash is added to the mother liquor, its sodium bisulfite is changed to sodium sulfite, and the suspension is soda ash in sodium sulfite solution.

[22] In Patent 1,023,179, the reaction is given as: $2NaHSO_3 + 2NaCO_3 + 2H_2O + 4SO_2 \rightarrow 6NaHSO_3 + 2CO_2$. The product is therefore held to be solid bisulfite of sodium, $NaHSO_3$, which is known to exist. In many processes, however, it is more likely that the anhydride, $Na_2S_2O_5$, forms, for several samples from different manufacturers contained 61.9, 64.1, 63.5, 62.8 per cent SO_2 respectively. Sodium bisulfite contains only 61.5 per cent SO_2, and as a contamination of sulfate is always present, and sulfite at times, it is probable that in some cases the product is anhydride, whose content of sulfur dioxide SO_2 is 67.3 per cent.

The neutral sulfite, Na_2SO_3, is made, for example, by the action of soda ash on the sodium bisulfite; it is sold both in the anhydrous form and as crystals, $Na_2SO_3 \cdot 7H_2O$. The production in 1939 was 11,213 tons of the two kinds together, with an average value of $62 a ton.

The absorbers are steel tanks lined with bricks, 15 feet high and 15 feet in diameter; the tight-fitting, closed top is cast-iron covered with lead. A 4-bladed hard lead propeller, working through a stuffing box, makes 100 revolutions per minute; the gas inlet pipe reaches about 1 foot below the liquid. A 10-inch main brings the gas, and 3-inch lines (3 to each tank) deliver it into the suspension. The spent gas from the first-stage absorber is pulled out by a fan and discharged into the air. The propeller shaft is lead-covered, as is also the rod carrying the plug valve which closes the discharge hole in the bottom.

Anhydrous bisulfite of sodium is used in the manufacture of dyes, and in their application to fiber; as an "antichlor"; in the sterilization of casks for beer and similar beverages, and for several other purposes.

Sodium Hyposulfite (Hydrosulfite)

Sodium hyposulfite, $Na_2S_2O_4$, called hydrosulfite in the trade, is a convenient form of the powerful reducer which is used for the reduction of certain dyes; before its advent in the trade, it had to be prepared at the textile mills and used at once. Formerly, it had to be imported, chiefly from Germany; it is now manufactured in the United States.

The method[23] includes four steps. (1) Powdered zinc of 93 per cent purity is suspended in water in a lead container provided with cooling coils and a stirrer. Pure sulfur dioxide, best from a tank of liquid sulfur dioxide, now an article of commerce,[24] is led in, fast at first, and more slowly near saturation. The temperature is kept below 30° C. The color changes to black, to gray, finally to cream.

$$Zn + 2SO_2(H_2O) \longrightarrow ZnS_2O_4(H_2O).$$

(2) The content of the saturator is transferred to a lead-lined steel tank, with stirrer; a soda ash solution is added, in slight excess over the amount indicated by the reaction

$$ZnS_2O_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2S_2O_4.$$

Zinc carbonate precipitates, while sodium hyposulfite remains in solution. The suspension is filtered on a stationary suction filter[25]; the cake is washed several times, but only the first wash is added to the filtrate; the subsequent ones are pumped into the saturator.

(3) The filtrate reaches the salting-out tank; its strength is adjusted to 15 per cent $Na_2S_2O_4$, and to this liquor salt (NaCl) is added, 300 grams for each liter of solution. The hydrated sodium hyposulfite, $Na_2S_2O_4 \cdot 2H_2O$, separates in the form of needles. The suspension is heated rapidly to 60° C. and kept there until all the crystals have been transformed to the

[23] "Sodium hydrosulfite as a dry powder," L. A. Pratt, *Chem. Met. Eng.*, 31, 11 (1924).
[24] Chapter 19.
[25] Chapter 42.

anhydrous sodium hyposulfite, $Na_2S_2O_4$, a sand-like, crystalline powder.[26] The crystals are allowed to settle, the supernatant liquor is run off, and hot denatured alcohol is added.

(4) The crystals suspended in the alcohol are transferred to a steam-jacketed vacuum pan, the alcohol sucked off after settling, and three portions of alcohol run in so that no water might remain. By warming and causing a vacuum, the adhering alcohol is removed (and recovered), leaving in the pan the dry, sandy material, of light gray color, 90 per cent pure.

The annual production of sodium hyposulfite, $Na_2S_2O_4$, may be estimated at not far from 20 million pounds. The current price (May, 1948) in large lots is $18\frac{1}{2}$ to 19 cents a pound.

Other Patents

U. S. Patent 1,946,089, on anhydrous (85 per cent) sodium sulfide, granular, free-running, and with rapid solution in cold water; 2,018,359, depilatory agent; 2,024,624, depilatory method and apparatus.

Problems

1. A sulfide furnace receives a charge of 1000 pounds of salt cake per hour; theoretically, 549.5 pounds of Na_2S should be recovered, but the recovery is only 77 per cent. The product is made into chip containing exactly 62 per cent Na_2S. How many pounds of chip are produced per day? The salt cake is never pure; the calculation must be based on a content of 95 per cent Na_2SO_4.

2. Sodium thiosulfate crystals $Na_2S_2O_3 \cdot 5H_2O$ of 97 per cent purity are produced by the reaction $2Na_2S + Na_2CO_3 + 4SO_2 \rightarrow 3Na_2S_2O_3 + CO_2$, from by-product liquor from the sodium sulfide process; the production of hypo crystals is 20,000 pounds per day. Assuming that the reaction takes place to the extent of 96 per cent, how many pounds of Na_2S, Na_2CO_3 and SO_2 will be required?

Reading References

"The manufacture of sodium thiosulfate," L. Hargreaves and A. C. Dunningham, *J. Soc. Chem. Ind.*, **42**, 147T (1923).

"Die Verfahren der anorganische chemische Industrie," zweites Berichtsjahr, Dr. W. Siegel, Berlin and Vienna, Urban und Schwarzenberg, 1935.

The patent and other literature as indicated in the text.

[26] The transition point of the hydrated salt to the anhydrous form is 52° C.

The manufacture of caustic soda directly from salt in solution, in a single operation, has passed, in the last forty years, from an exciting possibility to the humdrum of everyday technology. Caustic soda is a cheap, soluble alkali; lime is still cheaper, but is almost insoluble. Caustic soda is a strong alkali. Soda ash and ammonia are mild ones.

Chapter 5

Caustic Soda and Chlorine

Caustic soda, NaOH, a white solid, extremely soluble in water, is made by causticizing soda ash by lime and by the electrolysis of salt, NaCl, in water solution, with the simultaneous production of chlorine and hydrogen.

The production figures (U. S.) for the two main processes are given in Table 13.

TABLE 13.—*U. S. Production (1946) of caustic soda, expressed as 100% NaOH.**

	Short tons
Caustic soda by lime-soda process	
Liquid (60 and 75 per cent solution)	742,932
Solid	226,349
Total	969,281
Caustic soda by electrolytic process	
Liquid (50 and 75 per cent solution)	1,129,956
Solid	192,952
Total	1,322,908

* "Facts for Industry," Bureau of the Census.

1940 was the first year in which the production of electrolytic caustic exceeded that of lime-soda caustic.

CAUSTIC SODA BY CAUSTICIZING

Soda ash in the form of a 20 per cent solution is treated with milk of lime in slight excess, in a tank fitted with an agitator. The solution is warm (85° C.; 185° F.). After an hour, the agitator is stopped and the precipitated calcium carbonate settles; the strong (12 per cent NaOH) caustic liquor is decanted. Wash water is run into the agitator, and after some time is allowed to settle out its mud; the clear liquor is run off to the weak liquor tank. The mud is washed once more, yielding the "wash" which is run to the wash water tank. The mud is discharged from the tank; it may be carted to the dump, or it may be filtered and calcined, yielding a lime suitable for further causticizing. The first and second liquors are evaporated to 50 per cent NaOH concentration in single- or multiple-effect evaporators, and if solid caustic is desired, to the final strength of 98 per cent or better in cast-iron pots over a free flame. In many plants, the 12 per cent NaOH liquor is used directly.

It has been found that choosing the concentrations of the reacting liquors as stated gives a good conversion (98 per cent) in the reaction

$$Na_2CO_3 + Ca(OH)_2 \rightleftarrows 2NaOH + CaCO_3,$$

and yet does not impose too high a fuel cost for evaporation. The lime is

slaked with just enough of the wash water to form the hydrate, and then with only as much more as is required to make the milk; so prepared, the rate of settling of the calcium carbonate is 1.5 feet per hour instead of 0.28, when making the milk at once. Using a rotary slaker, the rate of settling becomes 7.81 feet per hour.[1] To utilize all the wash water, solid soda ash and the solid slaked lime may be fed into it.

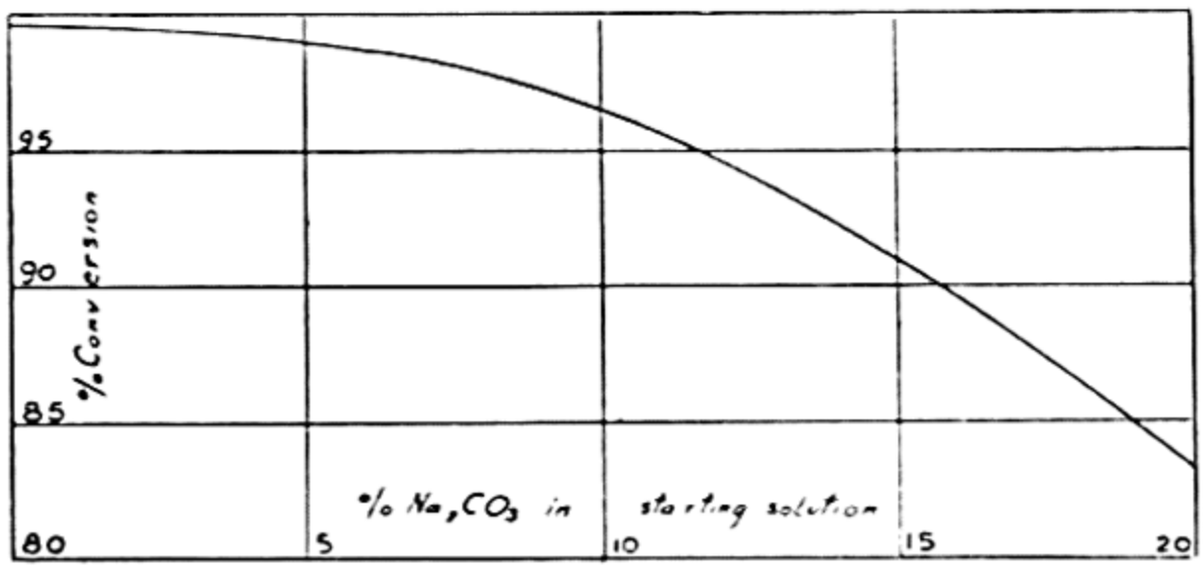


FIGURE 33.—The conversion of soda ash to caustic by lime, for various concentrations of the soda ash in the starting liquor. The lime added is $Ca(OH)_2$ with no additional water. Example: Starting with a 10% Na_2CO_3 solution, 96.5% of the sodium carbonate will be converted.

Instead of batch operation, which the description just given presents, continuous operation may be secured, with classifiers for purifying the milk of lime, and thickeners to hasten the separation of mud from clear liquor. The two best-known systems are the Dorr and the Mount. In the study of the evaporation of the caustic liquor to high strengths, the use of diphenyl vapors around a nickel tube was found promising.[2]

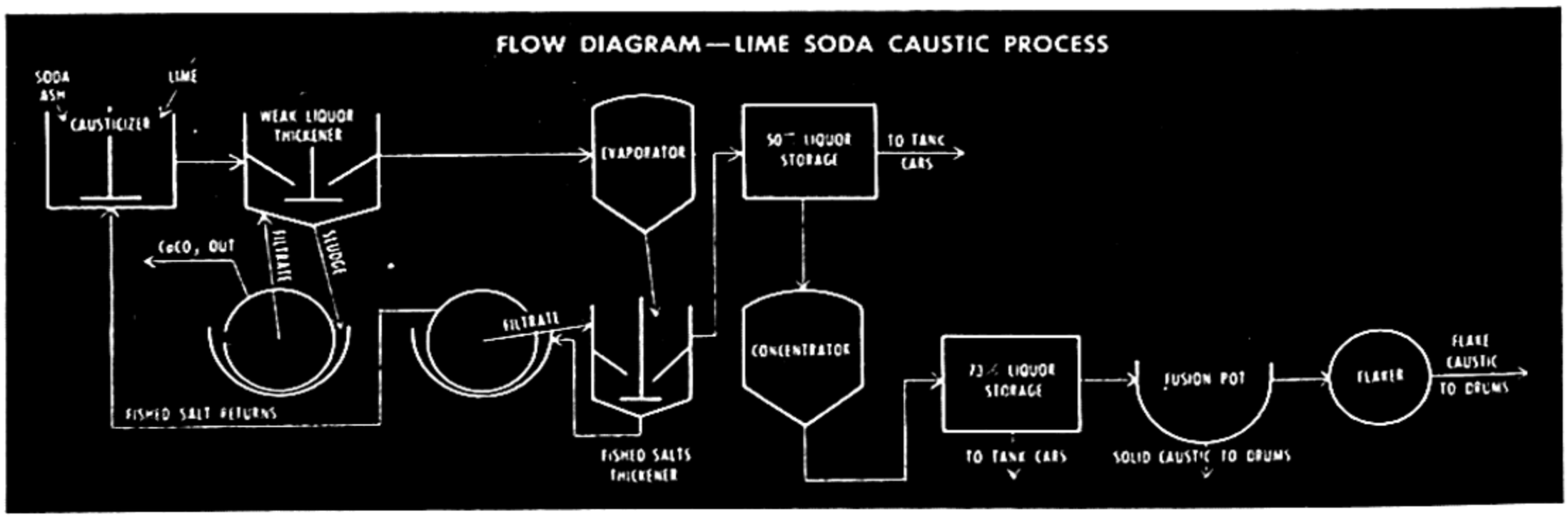


FIGURE 34.—A flow diagram for the lime-soda process for making caustic soda. (Courtesy Columbia Division, Pittsburgh Plate Glass Co.)

An analysis of caustic soda made by causticizing soda ash manufactured by the ammonia soda process, reveals that such caustic has a low chloride content, an important consideration in many uses. The composition is:

	Per Cent
NaOH	98.62
NaCl	0.30
Na_2CO_3	0.90
Na_2SO_4	0.18

[1] W. E. Piper, *Am. Inst. Chem. Eng.*, 24, 1 (1930).
[2] W. L. Badger, C. C. Monrad and H. W. Diamond, *Am. Inst. Chem. Eng.*, 24, 56 (1930).

Caustic Soda by Electrolysis of Brine

In tonnage, electrolytic caustic soda exceeds that made by causticizing; it represents, moreover, a totally different method of working, namely, the application of an electric current to chemical decompositions and regroupings.

Many cells have been devised in which the decomposition of salt in water solution may be performed. They may be listed under three heads: diaphragm cells; mercury cells, without diaphragm; and the bell-jar type, without diaphragm and without mercury. The first diaphragm cell was the Townsend cell, which is represented in modified forms by the Allen-Moore, Nelson, Gibbs, Vorce, Hooker, Dow Bi-polar, and other cells. The original mercury cell was the Castner, also the invention of an American, which is still used in its original form in one plant; other mercury cells in the United States include the Sorensen and the I.C.I.-Wyandotte. An important representative of the bell-jar type is the Billiter cell.

For all cells it is customary to purify the salt solution and to use it as strong as possible, that is, not far from saturated, about 25 per cent NaCl. The manufacture of caustic soda in diaphragm cells, in a few words, involves the preparation and purification of the saturated salt solution; electrolysis of this solution in the cell, wherein half the salt is transformed into caustic; concentration of this mixed solution with separation of the salt as the concentration rises; and final evaporation to anhydrous caustic over an open fire. For the mercury cells, the procedure is about the same, but the caustic liquor issuing from the cell is free from salt. This is an important advantage if the liquor is to be used on the spot: it requires no concentration, for the salt content need not be removed. The liquor issuing from the diaphragm cell, with as much salt as caustic, could not be used as such for most purposes. For the manufacture of solid caustic, this advantage disappears. The diaphragm cells produce a final caustic with 2 per cent NaCl; this small amount is not objectionable for the important applications of caustic. The great purity in this respect of caustic from mercury cells (0.004 per cent NaCl) does not bring it a premium. The general procedure for bell-jar type cells is similar to that for diaphragm cells.

The decomposition efficiency of cells varies between 50 and 60 per cent. Decomposition efficiency is the ratio of the salt decomposed to the total salt; thus if 6 parts of salt are decomposed into caustic, and 4 parts of salt remain unchanged in the liquor (both determined by titration), the decomposition efficiency is 60 per cent. The decomposition voltage for commercial cells lies betwen 3.5 and 5, with 4.5 perhaps an average. The theoretical decomposition voltage for NaCl in water solution is 2.25.[3] The voltage efficiency is the theoretical decomposition voltage divided by the actual decomposition voltage, here $2.25 \div 4.5 \times 100 = 50\%$. The actual voltage applied will vary with the current density desired, that is, the number of amperes per square unit of surface of electrode; the higher the current density, the higher the voltage necessary. A part of the difference in energy

[3] This value is based on the Gibbs-Helmholtz equation, and takes into account the heats of formation of the substances represented in the equation $NaCl + H_2O \rightarrow NaOH + \frac{1}{2}Cl_2 + \frac{1}{2}H_2$.

represented by the voltage figures appears as heat; the temperature of the diaphragm cell, for instance, maintains itself at about 60° C. In general, the rough estimate is made that the potential drop for each cell is 5 volts.

The current efficiency, or better, the cathodic current efficiency, varies from 90 to 96 per cent in the best-designed cells, under even running; it may drop to 75 per cent or even less, for a variety of causes. The cathodic current efficiency is the weight of caustic formed divided by the theoretical weight of caustic which the amount of current per hour (ampere hour, independent of voltage) should have formed (1.491 grams), multiplied by 100.[4]

The energy efficiency is the product of the voltage efficiency and the current efficiency, here $0.96 \times 0.50 \times 100 = 48\%$.

The amount of current required to liberate a gram-equivalent at each pole is the faraday, which is equal to 96,580 coulombs (1 coulomb = 1 ampere-second). One ampere-hour equals 3600 coulombs, so that the amount of material liberated by 1 ampere-hour is:

$$\text{Chlorine } \frac{3600}{96{,}580} \times 35.46 = 1.3218 \text{ grams}$$

$$\text{Caustic } \frac{3600}{96{,}580} \times 40.01 = 1.4913 \text{ grams}$$

The Electrolytic Cell

The two cells in Figure 35 show the essential parts of an electrolytic cell. The current, which is always direct current, is said to enter at the anode

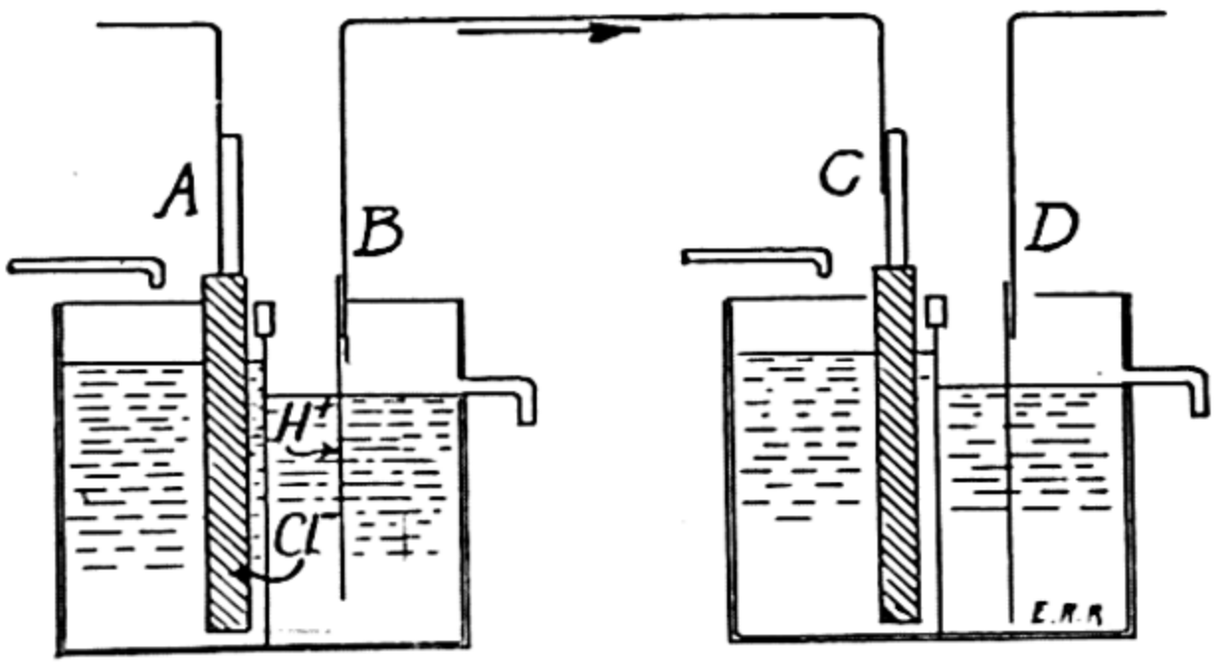


Figure 35.—Cells for the electrolysis of solutions of sodium chloride in water. The chloride ion, Cl^-, forms chlorine gas at the anodes, marked *A* and *C*; the hydrogen ion, H^+, forms hydrogen gas at the cathodes; the latter are marked *B* and *D*. A diaphragm divides the anode brine compartment from the cathode compartment.

and to leave at the cathode.[5] In a brine, there are present sodium ions (Na^+) and chloride ions (Cl^-), as well as ions resulting from the ionization of water, *i.e.*, the hydrogen ion (H^+) and the hydroxyl ion (OH^-). After the current is applied, the chloride ions give up their negative charge (one electron) and become yellow chlorine gas, Cl_2. The hydrogen ions acquire an electron each at the cathode, and form the hydrogen molecule (hydrogen gas). There are many more Na^+ ions than H^+ ions present at any time,

[4] Compare "The fundamentals of electrolytic diaphragm cells," by H. K. Moore, *Am. Inst. Chem. Eng.*, 13, I, 42 (1920).

[5] It would be more satisfactory to say that electrons enter at the cathode and leave at the anode, but the general custom will be observed.

but the single potential for hydrogen is lower than that for sodium.[6] As soon as the hydrogen ions present have deposited, more are formed by ionization of the water molecule, a process which takes place at a rate approaching the speed of light. The Na^+ ions thus remain undisturbed during the action of the current on the brine. The OH^- ions, constantly formed by the ionization of the water, accumulate at a rate which equals that of chlorine ion discharge, so that the Na^+ ions are matched in number by the newly formed OH^- ions. The reaction may be written:

$$Na^+ + Cl^- + H^+ + OH^- \rightarrow Na^+ + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2 + OH^-.$$

This is the process which goes on in the diaphragm cell. In the mercury cell, the deposition of hydrogen ions at the mercury cathode does not occur, because the mercury cannot accept them; here, the Na^+ ion functions, by acquiring an electron and dissolving as sodium metal in the mercury. In a second chamber, the amalgam first formed is "denuded" of its sodium, forming with water Na^+ again, and liberating hydrogen, which in turn leaves an equivalent number of OH^- ions to form the caustic soda in solution:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2.$$

Returning to the diaphragm cells, it should be noted that they are so connected that the current leaving at the cathode of one cell enters at the anode of the next. The path of the current lies through the metallic bar to

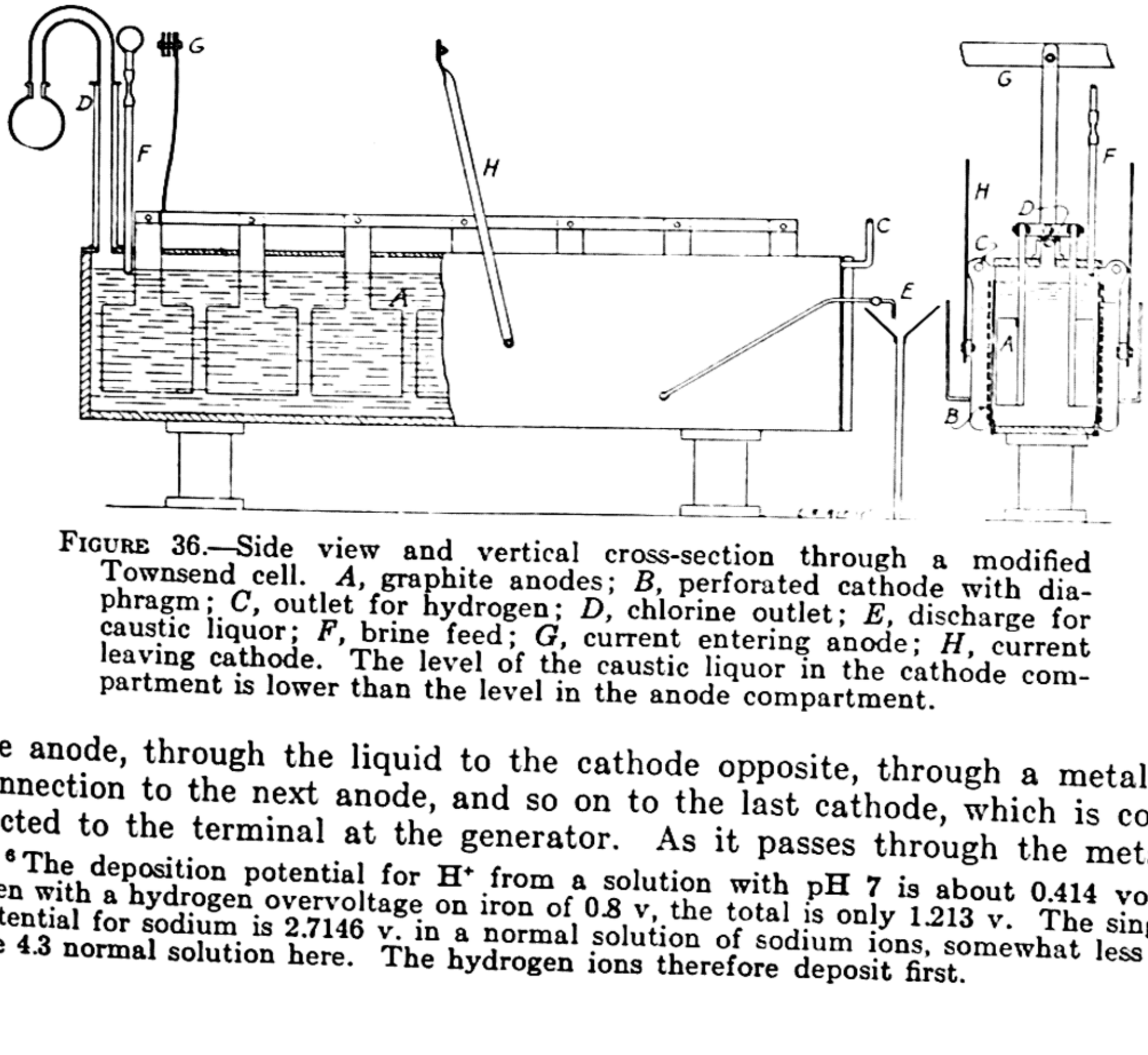


FIGURE 36.—Side view and vertical cross-section through a modified Townsend cell. *A*, graphite anodes; *B*, perforated cathode with diaphragm; *C*, outlet for hydrogen; *D*, chlorine outlet; *E*, discharge for caustic liquor; *F*, brine feed; *G*, current entering anode; *H*, current leaving cathode. The level of the caustic liquor in the cathode compartment is lower than the level in the anode compartment.

the anode, through the liquid to the cathode opposite, through a metallic connection to the next anode, and so on to the last cathode, which is connected to the terminal at the generator. As it passes through the metal,

[6] The deposition potential for H^+ from a solution with pH 7 is about 0.414 volt; even with a hydrogen overvoltage on iron of 0.8 v, the total is only 1.213 v. The single potential for sodium is 2.7146 v. in a normal solution of sodium ions, somewhat less in the 4.3 normal solution here. The hydrogen ions therefore deposit first.

the current causes no change (no chemical change); but as it goes through the brine, the decomposition takes place which has been described. In the Townsend cell, caustic gradually accumulates near the cathode; to prevent it from diffusing toward the anode, a well may be placed in the cell, forming two compartments. The wall allows slow passage of the solution and free passage to the sodium ions; by keeping the level in the anode chamber higher than in the cathode chamber, the hydrostatic flow is toward the cathode, nullifying the diffusion tendency of the NaOH toward the anode. The permeable wall is usually asbestos fibers supported on an ion screen, and is called the diaphragm.

Purification of the Salt Solution

The salt may be in the form of a natural brine, an artificial brine, or rock salt. The purification of the latter includes such steps as may be required for the brines. The salt is shoveled from the box car into an underground hopper feeding an inclined belt elevator or bucket elevator by means of which it is raised to the dissolving tank. This is kept filled, and warm water is pumped in at the base and allowed to overflow at the top; during its passage through the salt it becomes saturated. Instead of a wooden tank, a concrete tower (short) may be used. The brine is collected in the treating tank, where sodium carbonate is added in amounts just sufficient to precipitate the calcium and magnesium salts. After settling to remove the coarse suspended particles, the cloudy liquor is decanted periodically into a series of large, wooden settling tanks which act at the same time as storage. The tanks are in series, and the brine overflows very slowly from one to the next, so that they function as catch basins. The solution passing from the last basin is almost clear. It is filter-pressed; but the content of solid is so low that the press need be opened but once a week. Instead of filter-pressing, the brine may be filtered through a sand bed. The filtered salt solution, containing about 25 per cent NaCl, is elevated to a tank above the cells and fed through a constant-level boot to a 3-inch pipe with side branch for each cell. The method of regulating the amount fed to the cell varies considerably; one of the simpler schemes is to insert a horizontal plate with small orifice in the vertical branch leading to the anode compartment, with a glass sleeve immediately below the orifice plate to permit observation of flow. The size of the orifice determines the rate of flow.

Diaphragm Cells

All diaphragm cells embody the principle of enclosing the anode compartment by a diaphragm, as originally proposed by C. P. Townsend; therefore, they are all referred to as Townsend cells. However, the modified constructions of the later cells have been of the greatest importance; furthermore, they differ from each other radically. It is chiefly for convenience that they are grouped together under the same name. Of these modified Townsend cells, a sub-group would be formed by the Townsend-Baekeland [7] and Hooker cells, which are evidently related. Both have liquor in the cathode compartment, the kerosene in the Townsend-Baekeland cell

being replaced by caustic liquor, with a residual salt content, in the Hooker cell.[8] It seems certain that no cell remains in commercial operation with kerosene in the cathode compartment, so that the Hooker cell may be taken as typical of the diaphragm cells which have liquor in the cathode compartment.

The Hooker "S" Cell. Of the thirteen commercial diaphragm cells for caustic and chlorine, the Hooker "S" cell[9] has been the choice in almost

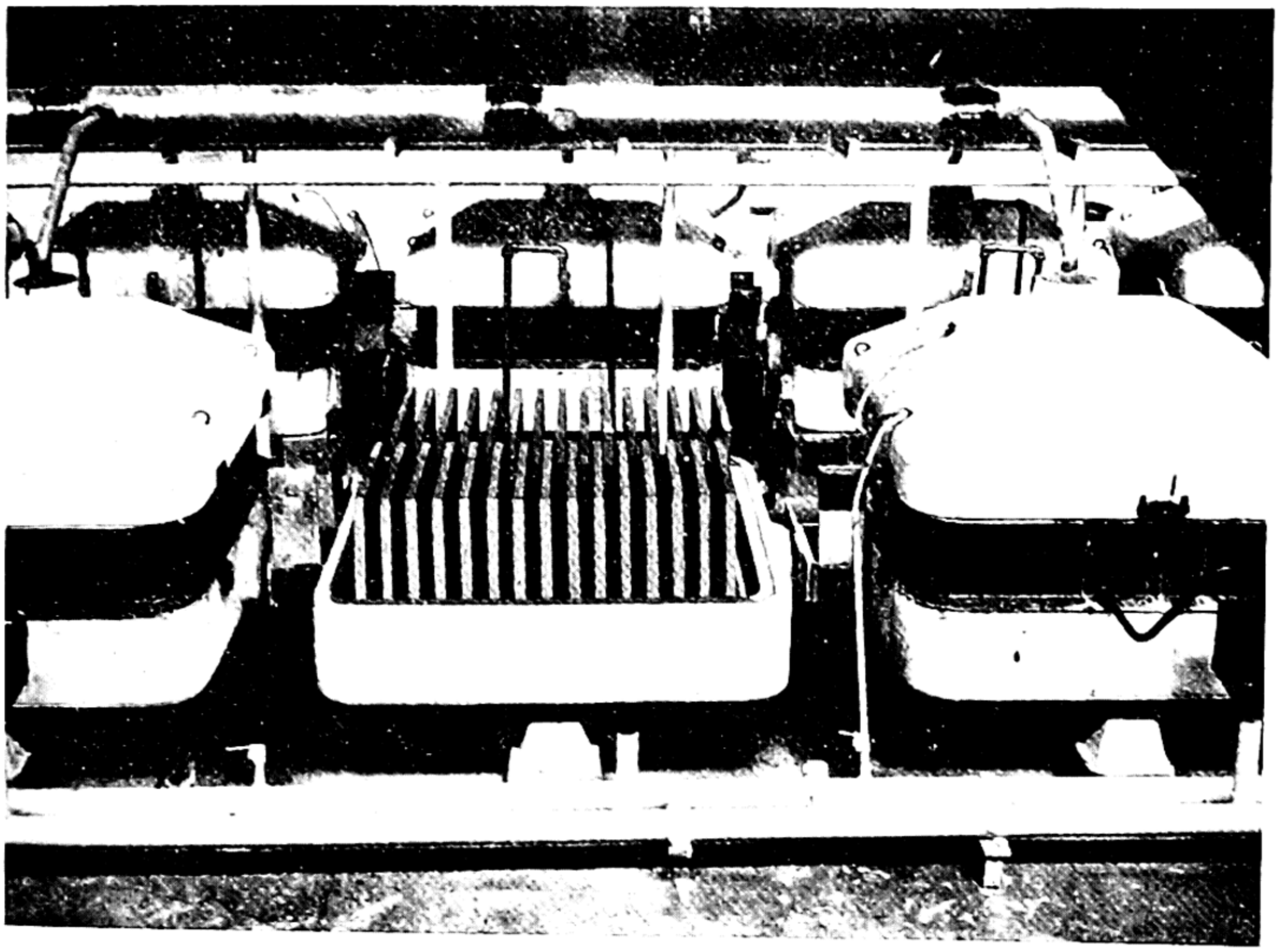


FIGURE 37.—The lower section of the Hooker "S" cell, showing the anode slabs in place. Note that the cell to the right carries a current connector at its middle section, and anode, the cell to the right has a connector to the rod in the lower section, an anode section. (Courtesy Hooker Electrochemical Co.)

half the installations in the recent past (24 out of 54). It is a large cell, in terms of amperage, yet it occupies but little floor space; originally a 5000-ampere cell, it is now generally made in the 10,000-ampere size, and this is the standard at present. There are in operation several 20,000 ampere Hooker "S-3" cells, and larger ones are being discussed. The 10,000-ampere size is likely to remain the most popular. By contrast, a circular cell, with merits of its own, such as the Vorce cell, is a 1000 or 1500-ampere unit.

The Hooker "S" cell is essentially square in cross section. It consists of a concrete top piece, a concrete bottom piece (set on short legs) a central steel frame which carries the iron wire mesh forming the multi-fingered cathode.[10] The latter is also the support for the asbestos diaphragm, an unbroken mat formed by plunging the steel cathode into a suspension of

40 pounds of asbestos fibers in cell liquor and applying suction to the cathode chamber. The anode is part of the bottom section. It is made of impregnated graphite slabs set in a bitumen-covered lead base plate which receives the current; the slabs reach up from below between the fingers of the cathode, so that every vertical face of the cathode and diaphragm is close to a similar graphite surface. A single broad-faced connection at the cathode of one cell carries the current the short distance to the single stout rod feeding the anode of the next cell. The construction will be clearer after examination of Figure 39. The cell, closely packed as it is with anode and cathode branches, has a 4-inch central passage for anolyte circulation.

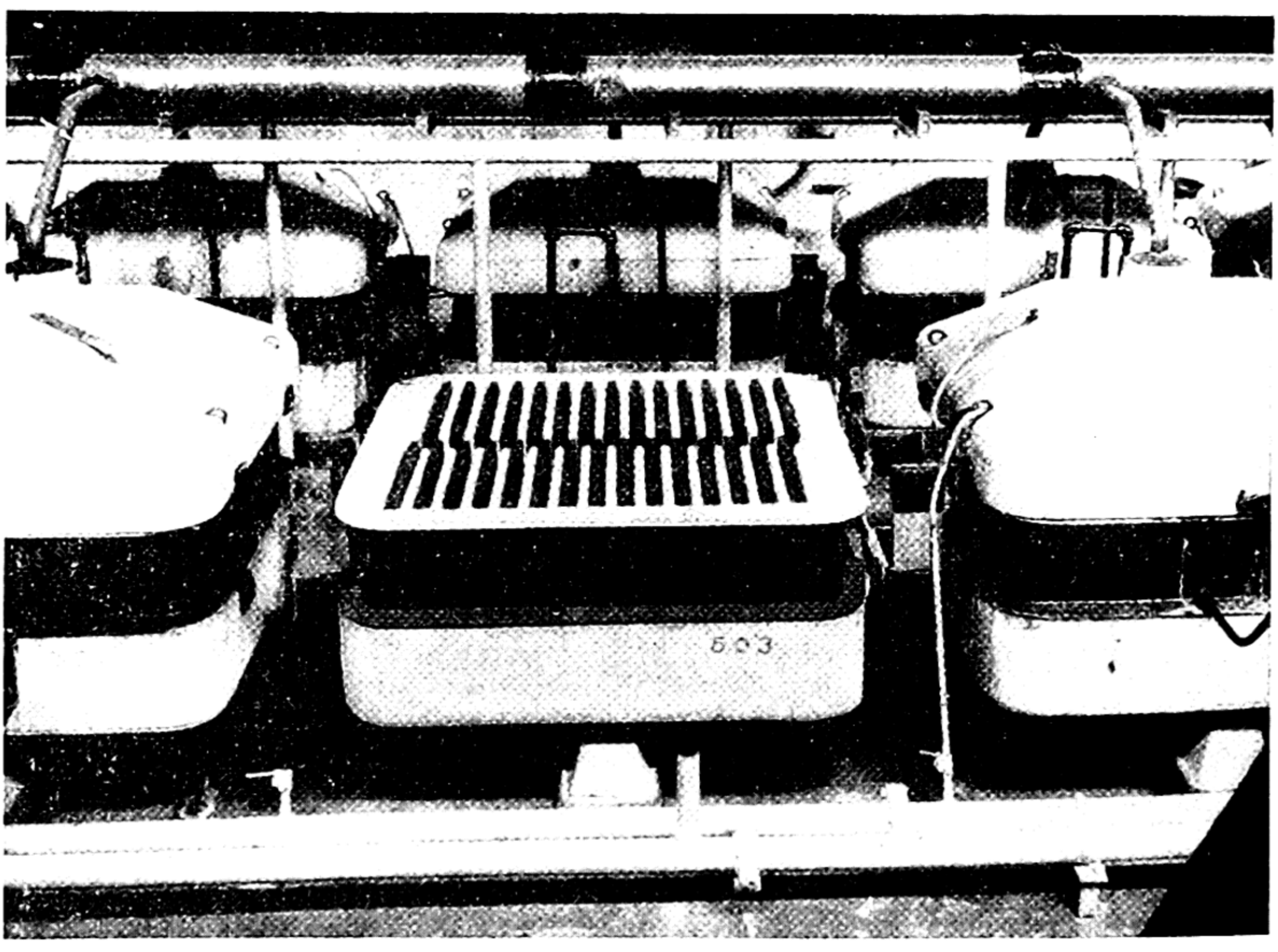


FIGURE 38.—View of the Hooker "S" cell with the middle section, the cathode section, in place. Note the chlorine line at the top of picture, with branch line from each cell. At the bottom are two lines, the brine line, the inner one, and the caustic line. (Courtesy Hooker Electrochemical Co.)

The brine is preheated to 60° C. (140° F.) and enters the cell in the dome (see sketch); the stream of brine breaks into drops, so that there is no electrical conductivity from the cell to pipes and heaters outside the cell.

[7] "The new electrolytic alkali works at Niagara Falls," Leo Baekeland, *Electrochemical and Metallurgical Industry*, **5**, 209 (1907). *Also* **7**, 313 (1909), by the same author.

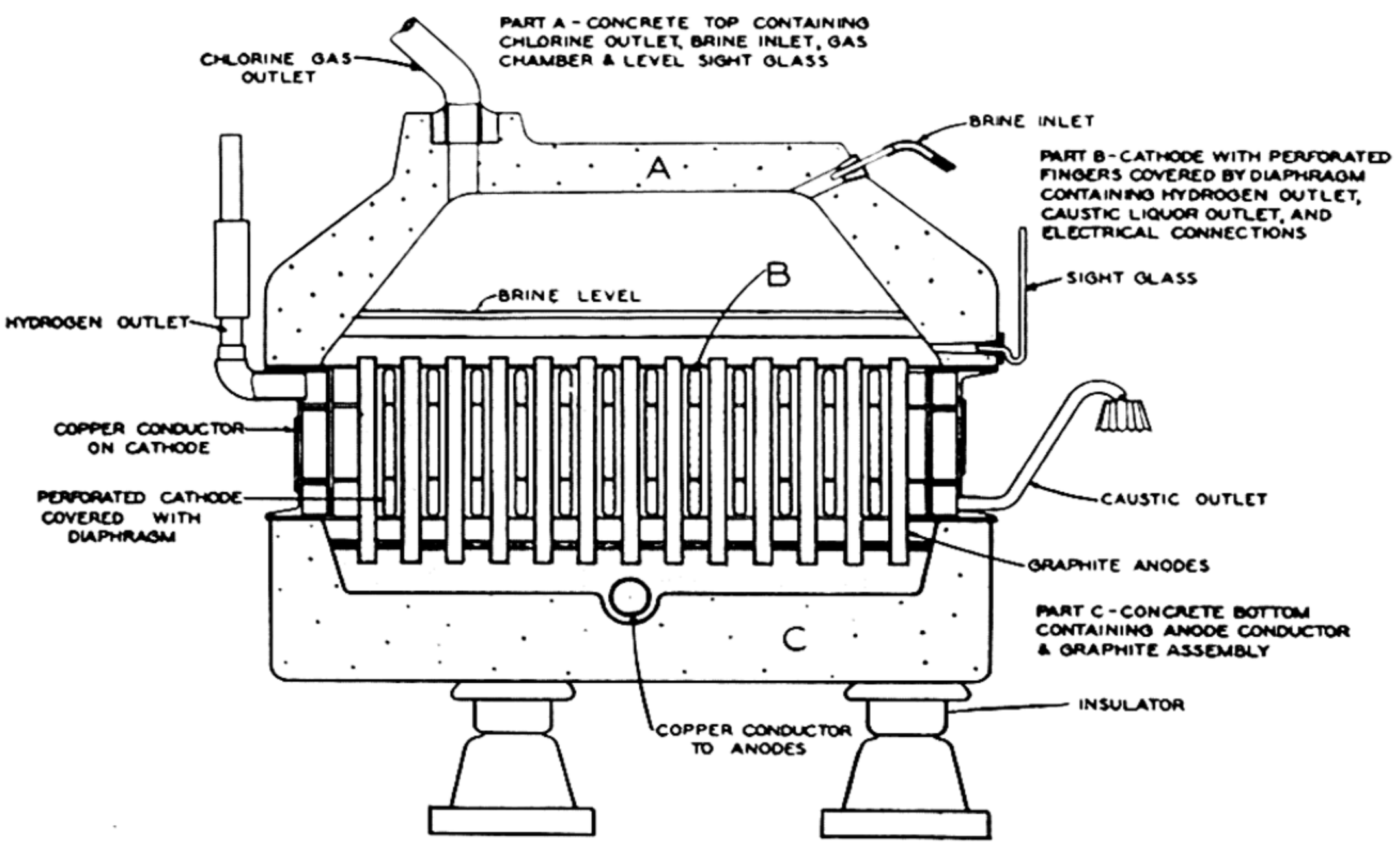
[8] "Description and views of the Townsend cells and the Niagara Falls plant of the Hooker Electrochemical Company," A. H. Hooker, *Trans. Am. Chem. Eng.*, **13, I**, 55-60 (1920).

[9] U. S. Pat. 1,866,065, with 6 sketches.

[10] U. S. Pat. 1,862,244; 1,865,152.

Its content of salt (NaCl) is 322 grams per liter, essentially a saturated solution. The cell works at a temperature of 90° C. (194° F.). The chlorine gas outlet is in the dome, a stoneware pipe connected to a larger stoneware header. The hydrogen leaves the upper level of the cathode chamber through an iron pipe, insulated by a rubber sleeve coupling. The caustic dribbles out from the lower part of cathode chamber through an adjustable outlet, so that the level of caustic in the chamber can be controlled.

The voltage drop per cell when the cell is new is 3.4 volts; as time passes, the anode surfaces become imperfect, and the voltage gradually rises to a



DIAGRAMMATIC SECTION
HOOKER TYPE 'S' CELL

FIGURE 39.

final 4.4, when the anode section is renewed. The current density [11] at the anode for the 7000-ampere cell is 0.446 ampere per sq. in., and at the cathode, 0.377 ampere per sq. in. The level of the brine may be observed by means of a sight glass; as the cell ages, it rises, producing a higher head, in order to overcome plugging in the diaphragm and maintain a given flow of cathode liquor. The diaphragm is replaced on an average of 4 times per anode run. The life of the anode section is about 365 days. In the 10,500-ampere cell, the loss of graphite averages about $5\frac{1}{2}$ pounds per ton of chlorine produced. The construction of the cell is such as to allow the vertical removal of the upper section and of the cathode section, a feature which saves floor space. As spare sections are always in readiness, a change can be made in a few hours. The energy efficiency is 65 per cent; the ampere efficiency is of the order of 97 per cent.

[11] The current density means the current in amperes per unit surface. An increase in current density requires an increase in voltage.

At the higher temperature of operation,[12] chlorine is less soluble in the anolyte, and a smaller amount of chlorate forms.

The caustic liquor produced contains on an average 11.3% NaOH, 15% NaCl and 0.1% $NaClO_3$. The gas in the chlorine header contains on a dry basis, 97.5% Cl_2, 1.4% CO_2, 0.8% O_2, 0.2% H_2 and 0.1% N_2. The hydrogen gas, except for moisture, is essentially pure; it is under a slight positive pressure. The chlorine line is under a slight negative pressure.

The 10,500-ampere cell produces 790 pounds of caustic (NaOH), 685 pounds of chlorine and 3560 cubic feet of hydrogen per day.

FIGURE 40.—A recent installation of Hooker "S" cells. (By permission.)

Nelson Cell. In the Nelson cell, as also in the Allen-Moore, Gibbs, Vorce, and several other cells, the cathode compartment contains no liquor; the caustic solution, with residual salt, runs down the diaphragm and collects at the base. In the Nelson cell,[13] steam is sent into the cathode space to maintain the temperature near 65° C. (149° F.). The form of the cell is again a narrow rectangular box set up as the Hooker cell is; the Allen-Moore has a similar outside appearance. There is only one row of suspended graphite anodes, and the usual size unit receives 1000 amperes; the current density is 50 amperes per square foot, half of that in the Hooker cell. The voltage is lower, averaging 3.7 volts. Among other advantages, this cell produces a very pure chlorine; for this reason it was chosen for the installa-

[12] The higher the temperature, the less the resistance; higher than 90° C. is avoided because of the greater action of the products on the cell walls.

[13] *Trans. Am. Electrochem. Soc.*, 35, 239 (1919), or U. S. Patents 1,149,210 (1915) and 1,149,211.

tion at Edgewood arsenal during the first World War [14]: 3500 Nelson cells furnished 100 tons of chlorine per day; the anodic ampere efficiency (for chlorine) was 90 per cent; the caustic liquor was maintained 10 to 12 per cent NaOH and 14 to 16 per cent NaCl.

Allen-Moore Cell. The Allen-Moore cell [15] has usually 1200 ampere units, working with a voltage of 3.6; the cathodic current efficiency is maintained at 95 per cent over extended periods. The caustic liquor contains 8 to 10 per cent NaOH and about 12 per cent NaCl. The cell is constructed of concrete and cast-iron sides, and has in general the shape of a narrow

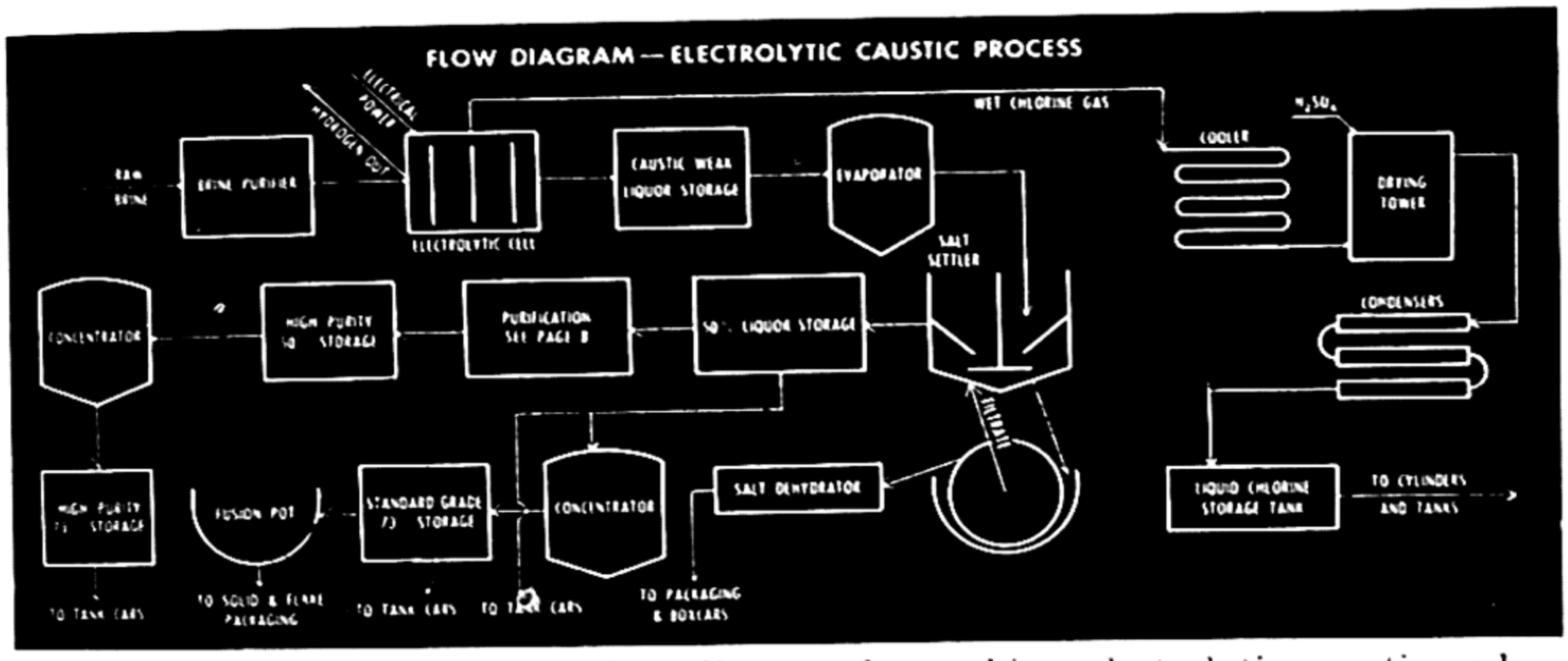


FIGURE 41.—A more complete flow diagram for making electrolytic caustic soda and chlorine. (Courtesy Columbia Division, Pittsburgh Plate Glass Co.)

rectangular box. The basic principle of the unsubmerged cathode, that is, of using an empty cathode compartment, was first proposed by the designers of the Allen-Moore cell.[16]

The cell described by L. D. Vorce [17] is cylindrical, and is said to furnish more caustic per square foot of floor space than any other cell. Another cylindrical cell used in Canada, and by the United Alkali Company of Great Britain, is the Gibbs cell,[18] patented in 1907.[19, 20] The units are of 1000-ampere capacity, requiring 3.6 volts; the floor space occupied is small.

The Hargreaves-Bird cell produces sodium carbonate solution. The caustic soda primarily formed is changed to the carbonate at once by carbon dioxide and steam injected into the cathode compartment. The Griesheim cell has magnetic anodes, and solid salt is fed into the anode liquor.

CONCENTRATION OF THE CAUSTIC LIQUOR

The liquor flowing from the cathode compartment contains both caustic and salt, for the diaphragm cells just discussed. The solution con-

[14] "The U. S. Government chlorine-caustic soda plant at Edgewood arsenal, Edgewood, Md.," Samuel M. Green, *Chem. Met. Eng.*, 21, 17 (1919).
[15] "The Allen-Moore cell in the pulp and paper mill," F. H. Mitchell, *Chem. Met. Eng.*, 21, 370 (1919).
[16] *Trans. Am. Inst. Chem. Eng.*, 13, I, 11 (1920).
[17] *Trans. Am. Inst. Chem. Eng.*, 13, I, 47 (1920), and U. S. Patent 1,286,844.
[18] *Ind. Eng. Chem.*, 16, 1056 (1924).
[19] Brit. Patent 28,147, also U. S. Patent 874,064.
[20] In its original form, the Gibbs cell had caustic liquor in its cathode compartment.

tains about 12 per cent NaOH and 12 per cent NaCl. It is concentrated in a double-effect evaporator,[20a] for example, and each boiling pan may have its own separator in which the salt is collected as fast as it separates from solution, so that the heating surface in the pan may always be swept by liquor. When a batch of cell liquor has been concentrated to 50 per cent NaOH, only 1 per cent of salt remains in the solution. The suspension from pan and separator is pumped to a settler with Monel wire over a conical base; the salt settles on the wire, the caustic liquor collects in the cone. The liquor passes to cooling tanks, where any salt in suspension is carefully removed

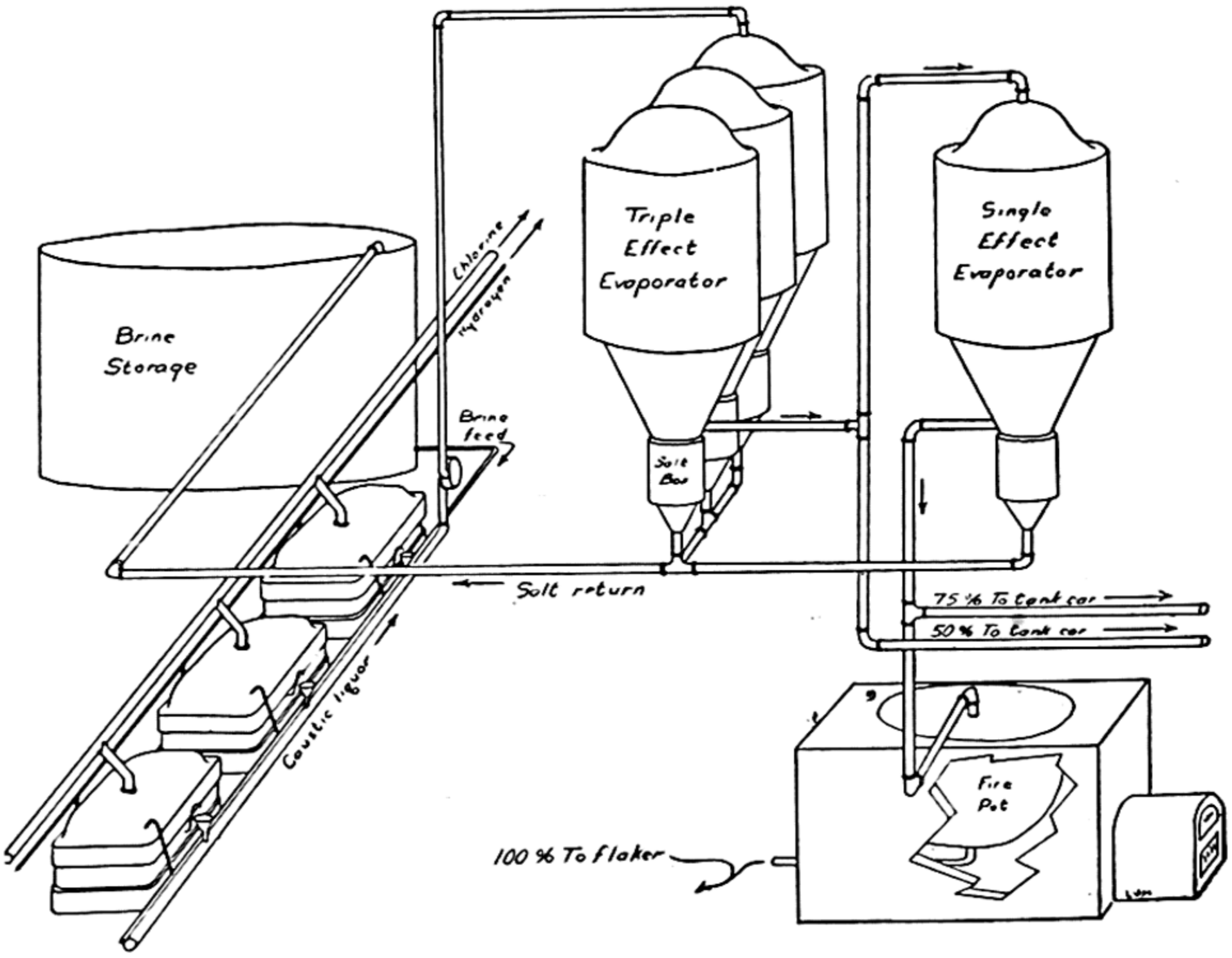


FIGURE 42.—Flowsheet for production of 50 per cent, 70 per cent and solid caustic soda from the liquor formed in diaphragm caustic cells working on brine. The production of hydrogen and chlorine is indicated.

by settling. The 50 per cent NaOH liquor is concentrated further in some plants to a 70 per cent concentration in a single vacuum pan heated with high-pressure steam. The liquid caustic, which is sold as such, offers several advantages: it may be handled in pipes; no drum containers are necessary; less labor and less fuel are required in its production in comparison with solid caustic; and it is in the form in which the customer applies it. The caustic produced and sold in liquid form (50 and 70 per cent NaOH) in 1946 was almost six times as much as that sold in solid form. In order to produce the latter, the 50 or 70 per cent is boiled down in cast-iron pots heated by an oil fire, until all the water is evaporated. The liquid anhydrous caustic, with perhaps 2 per cent NaCl, is removed from the pots by a

[20a] Chapter 43.

centrifugal pump lowered from a crane.[21] The liquid caustic is pumped to thin steel drums on low trucks; after cooling, the mass is solid. The weight of a caustic drum is generally 700 pounds net. The anhydrous caustic is also produced in crushed form; in flakes. Experiments on a pilot plant scale have been reported in which the caustic soda is dehydrated to a free-flowing powder by concentrating in the presence of kerosine.[22]

The salt in the settlers is washed a number of times by liquors of decreasing caustic content; it is made up to a soft mush and pumped to the dissolver, re-entering the system with the raw salt solution.

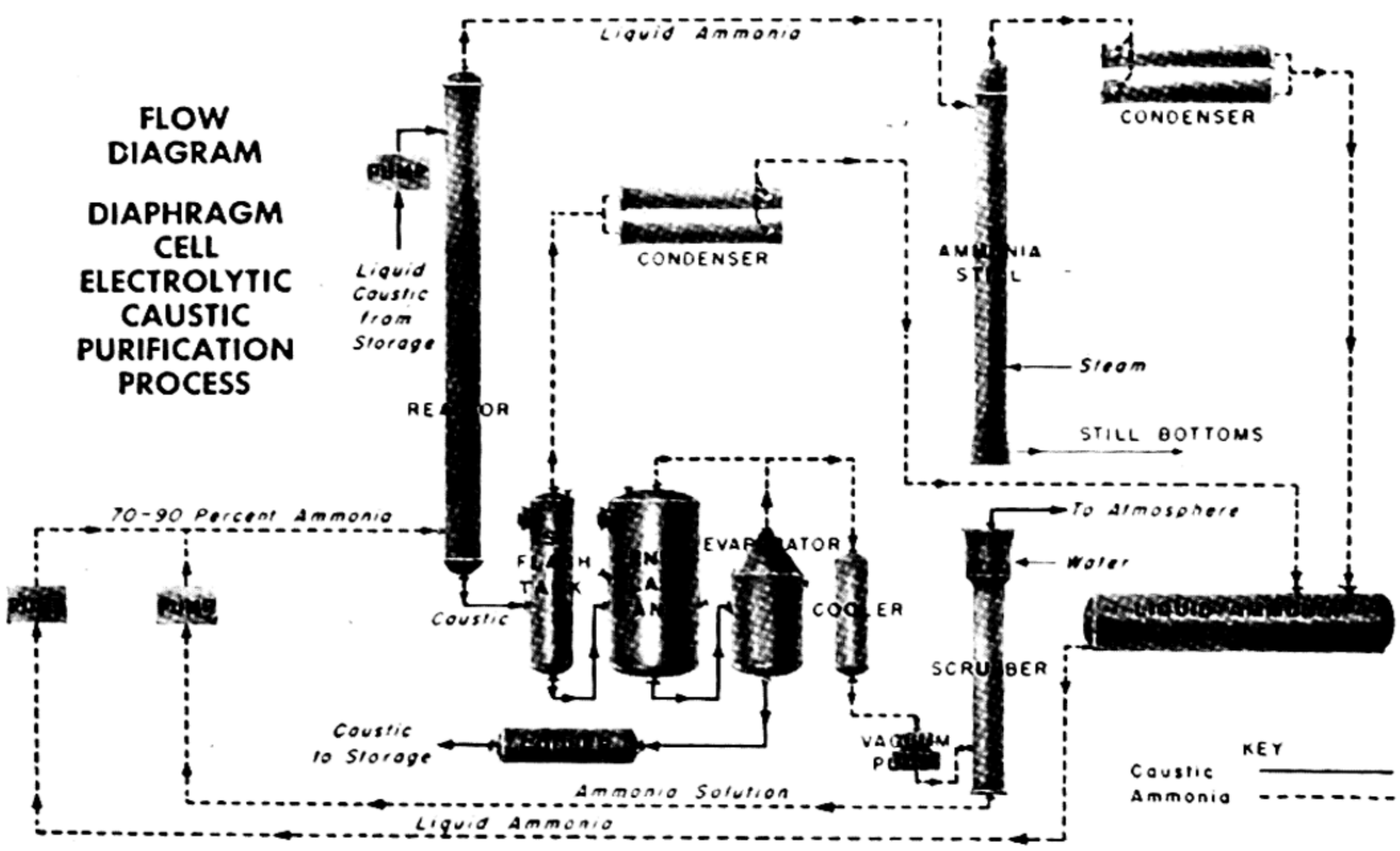


FIGURE 43.—Purification process for diaphragm caustic liquor, using anhydrous ammonia as extracting medium. (Courtesy Columbia Division, Pittsburgh Plate Glass Co.)

More and more evaporators are being equipped with nickel tubes, and also with nickel-clad walls wherever they come into contact with caustic liquors. The time is coming when caustic will be evaporated to the anhydrous state in nickel-clad evaporators with nickel tubes, using a high-temperature heat transfer agent, such as "Dowtherm" (diphenyl and diphenyl oxide).

For use in making viscose rayon, a caustic soda with a low chloride content, such as 0.15 per cent NaCl on the 100 per cent basis, is required. The excess NaCl in the caustic liquor from diaphragm cells may be reduced in one of several ways: (1) Hydrates such as $NaOH \cdot 3.5H_2O$ and $NaOH \cdot 2H_2O$ may be crystallized in jacketted crystallizers with agitators, and the crystals filtered off; the liquor carries away the bulk of the sodium chloride. (2) A triple salt may be formed by adding sodium sulfate, which binds NaCl

[21] *Ind. Eng. Chem.*, 16, 1057 (1924).
[22] *Ind. Eng. Chem.*, 32, 154 (1940).

as $NaOH \cdot NaCl \cdot Na_2SO_4$, insoluble in 35 per cent caustic solution, and on filtering, removes it.[23] (3) Liquid ammonia may be used for the extraction of NaCl and the small amount of sodium chlorate, $NaClO_3$, present.[24] In general, there is no difficulty in selling caustic from diaphragm cells in the low-chlorine caustic market.

The Mercury Cell

In the mercury cell working on brine, the cathode consists of mercury, and the anode of graphite, as before. There is no diaphragm. The salt in solution is decomposed, as already stated, the sodium ion accepting an electron and forming a sodium metal ion, which dissolves in the mercury.

The chlorine is liberated, as before, in the form of a yellow gas. These events take place in one of the chambers of the cell, the electrolyzing chamber. The amalgam is then transferred, by tilting the cell, by pumping, or in other ways, to the denuding chamber containing water, where the sodium metal reacts to form hydrogen gas and a solution of caustic,

$$2Na + 2H_2O \rightarrow 2NaOH + H_2.$$

In the original form of the Castner cell,[25] the removal of the amalgam to the denuding chamber is by tilting, about once a minute, through a distance of one-half inch. The cell consists of a low box with three long chambers; each of the two electrolyzing compartments has a graphite anode and mercury cathode; an iron grid on legs rests over the amalgam layer. The longitudinal partitions reach into grooves which the mercury seals, but past which it can travel on tilting. Other details are: rich brine enters the electrolyzing compartment, and depleted brine leaves it; the denuding chamber receives water, while the caustic solution leaves it. The units are 1000-ampere units, the voltage being about 4; a liquor containing 35 per cent NaOH is generally obtained.[26] Further concentration of the caustic, when performed, is greatly simplified by the absence of salt.

In the United States, the mercury cells now installed are the Sorensen and the I.C.I.-Wyandotte. Only a small percentage of installed capacity for chlorine and caustic is of the mercury cell pattern. It is different in Germany, where over the period which ended with World War II, 59 per cent of the chlorine production was by means of amalgam cells, compared to our 4.3 per cent.[27] The German cells which received most attention are very large in size and in amperage: the 7-meter horizontal, flat mercury cell (I. G. Farben, Höchst) operates at 13,000 amperes normally and at 16,000 in emergencies; the drum-type vertical mercury cell (also I. G. Farben) in various large sizes runs as high as 40,000 amperes. In the latter cell,[28] the cathode is a steel drum with 5 circular disks, which turn in an appropriate space with the anodes as walls (upper part). The speed of rotation is

[23] Ger. Pat. 522,676; U. S. Pat. 1,888,886 and 1,998,471.
[24] *Chem. Met. Eng.*, p. 119 (August, 1944).
[25] *Electrochem. Ind.*, **1**, 11 (1902).
[26] *Chem. Ind.*, **61**, 45 (1947).
[27] "Diaphragm vs. Amalgam Cells" (for chlorine-caustic production), Robert B. MacMullin, *Chemical Ind.*, **61**, 41 (1947)
[28] *Chem. Eng.*, **53**, 113, (1946).

7 r.p.m. The lower part of the drum contains mercury, through which the cathode disks travel in the lower half of their path. The steel cathode becomes coated with mercury, which accepts the discharged sodium, carrying it into the basin of mercury where it distributes itself as a dilute amalgam. The amalgam is pumped into the decomposer where water reacts with the sodium, giving caustic and hydrogen; the mercury then returns to the cell.

The Krebs mercury cell, as used in Sweden, is a long cell which takes up to 15,000 amperes.

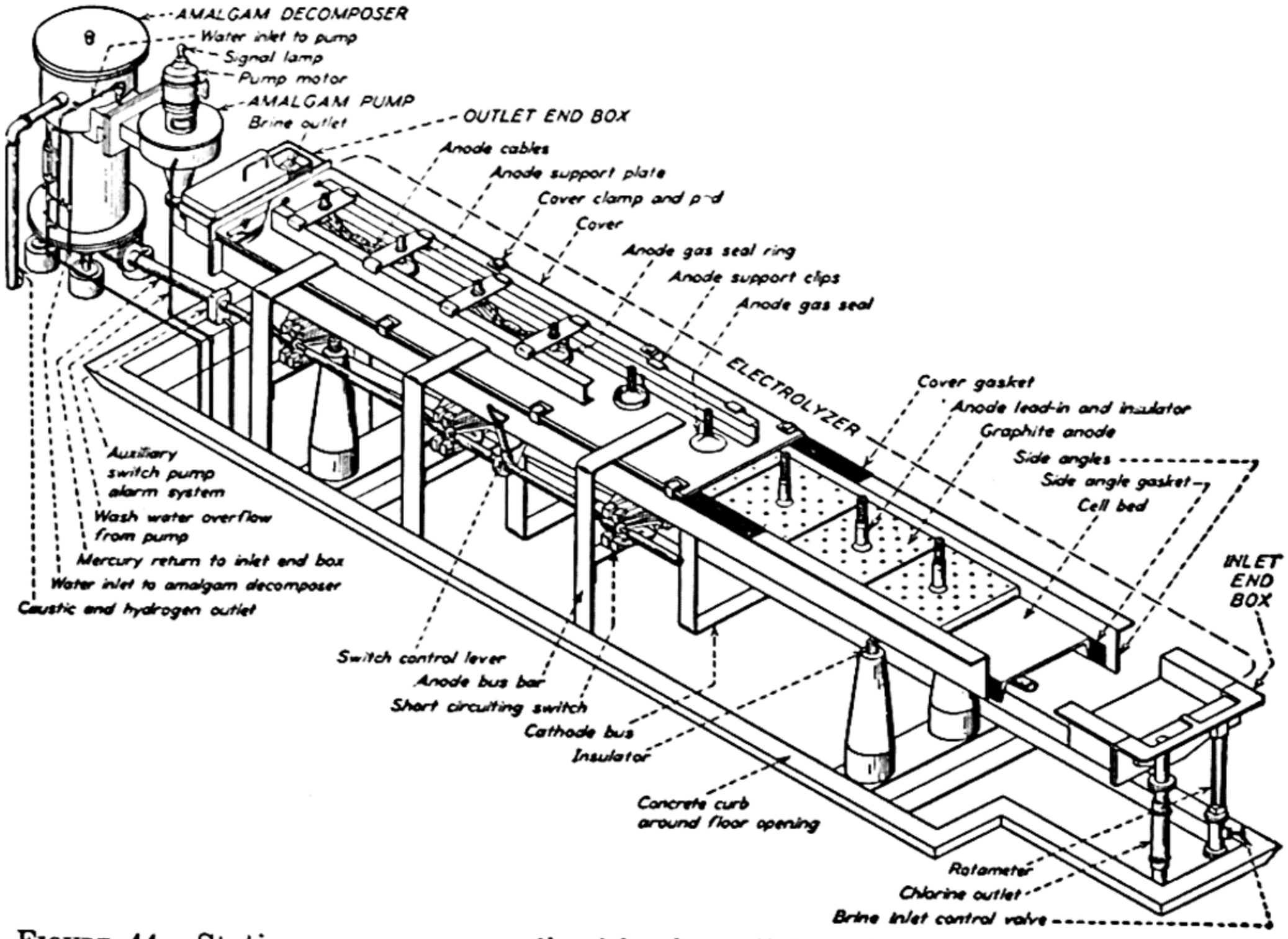


FIGURE 44.—Stationary mercury cell with electrolizing chamber separate from decomposing chamber. (By courtesy of Mathieson Chemical Corp., N. Y.) (Reproduced from *Chemical Engineering*, 54, (1947) by permission.)

A new mercury cell,[29] installed at Arvida, in Quebec, Canada, is operating successfully. It has a long, narrow electrolyzing chamber; the amalgam passes to a smaller, tower-type, cylindrical decomposer where pure water is fed in to make caustic solutions containing up to 50 per cent very pure NaOH. A pump functions between the electrolyzer and decomposer.

The relative merits of the two types of cell have been discussed in the literature.[27] If pure caustic is required, with 0.004 per cent NaCl, the mercury cell is the proper choice. The caustic made in diaphragm cells may be purified, as previously stated, so that the normal 1 per cent NaCl, in 50 per cent NaOH solution, becomes 0.16 per cent. Well worth considering is a co-ordinated operation of diaphragm and mercury cells.

The Bell-Jar Type Cell. In the Billiter cell,[30] the graphite anode is sus-

[29] "New mercury cell makes its bow," W. C. Gardiner, *Chem. Eng.*, 54, 108 (1947).
[30] British Patent 11,693 (1910).

pended in a bell-like housing, from which the chlorine is drawn off; the cathode consists of a number of iron rods slightly inclined from the horizontal; each rod is surrounded by a tight asbestos tube. At the edge of the jar, the rods and tubes rise upward; as the hydrogen is evolved along the rods, it travels upward, carrying with it the caustic liquor, which is delivered to a small receiving chamber in each cell, from which it is sent to the evaporators. The brine entry into the bell is such that the flow is toward the cathode, and as the caustic is carried out as fast as formed, it does not interfere with the passage of the current.

The estimated distribution of caustic soda sold in the open market is given in Table 14.

TABLE 14.—*Estimated distribution of caustic soda consumed in the United States (1947).**

	Short tons
Chemicals	460,000
Rayon and transparent film	455,000
Petroleum refining	160,000
Pulp and paper	130,000
Lye and cleaners	120,000
Soap	110,000
Textiles	105,000
Rubber reclaiming	27,000
Vegetable oils	20,000
Exports	130,000
Miscellaneous	363,000
Total	2,080,000

* *Chem. Eng.*, Feb., 1948.

The prices to consumers in 1946 were: solid in drums, $55 a ton; flakes, $60; as 47-49 per cent liquor, $42. The quotations in 1948 (May) are as follows: Solid caustic, drums, $47; flakes, $65; in liquid form, as 70 per cent, $47; as 50 per cent, $43; rayon type as 50 per cent, $45.

Potassium hydroxide is made successfully from potassium chloride in the Hooker "S" cell, with chlorine as by-product. A method for dissolving the solid chloride in the original shipping container, such as a liquid-tight cartanks with several manholes, so that solution only need be handled, has been patented.[31] The method is applicable to any other salt or material which is soluble. Caustic potash in flake form, low-chloride, was quoted (May, 1948) at $192 to $195 a ton.

BY-PRODUCTS OF ELECTROLYTIC CAUSTIC SODA

Hydrogen from the cathode chamber and chlorine from the anode chamber are the by-products of electrolytic caustic soda. In a chemical center such as Niagara Falls, N. Y., any surplus is sold to other industries and the demand is sufficient to justify a hydrogen pipe distribution system. The chlorine may be burned in an excess of hydrogen to give extremely pure synthetic hydrogen chloride, which, dissolved in water, gives hydrochloric acid. A submerged combustion burner has been described recently.[32] The

[31] U. S. Pat. 2,143,273.

[32] "Synthetic hydrogen chloride," Aylmer H. Maude, *Chem. Eng. Progress*, 44, 179 (1948).

hydrogen is largely used in catalytic hydrogenation. The chlorine, however, is the more important by-product of the two; it is produced at an ever-increasing rate. In 1946, 1,165,126 short tons were produced, while in 1947 the production reached 1,375,000 tons for chlorine from all sources. The chlorine is produced mainly in electrolyses of brine, of magnesium chloride, and of fused salt (NaCl). An amount estimated to be 185,000 tons [33] stems from the nitrosyl chloride process, and from the electrolysis of potassium chloride.

There are market conditions which alter the relation between caustic soda and chlorine, so that the first product of the cell is more truly chlorine, while the caustic is the by-product.

Liquid Chlorine. Gaseous chlorine is easily changed to a brown liquid; this circumstance has extended its usefulness considerably over that of the gas. At 0° C. (32° F.), a pressure slightly over 39 pounds will cause liquefaction; at −20° C. (−4° F.), slightly over 12 pounds is needed; at −33.5° C. (−28.5° F.), only a little over atmospheric pressure is required. A temperature of −20° C. may be obtained with an ammonia refrigerating system, brine or gas, while −40° C. (−40° F.) is obtained by a carbon dioxide system (Chapter 12).

The chlorine gas leaves the anode compartment warm and moist. An analysis of the raw gas is given on page 98. Leakage of hydrogen into chlorine is carefully guarded against because the two gases form explosive mixtures. The chlorine gas passes along a 3-inch stoneware line to a stoneware or quartz S-bend cooled by water; this is followed by a second cooler in which refrigerated brine is used; or a series of two stoneware Hart condensers, one being cooled by water, the second by cold brine, may be used. The cold gas then enters an Edgewood drying tower, with several sections, down which 98 per cent sulfuric acid travels. The Edgewood tower has displaced the Cellarius vessels and the disk cooler. The gas next reaches a Nash [34] Hytor, a turbo-blower, whose multibladed impeller works in sulfuric acid held in an elliptical casing. For each revolution, there are two compressions and two expansions of the working fluid caused by the shape of the casing; the alternate compression and expansion move the gas. A pressure of 15 pounds—in the special models recently developed, of 30 pounds—can be obtained. The compressed gas is cooled in double-walled tubes, through the inner passage of which liquid carbon dioxide is expanding. The chlorine liquefies at a rapid rate, and is led to a steel storage tank. Any of the less compressible gases present as impurities, such as carbon dioxide, carbon monoxide and hydrogen, are vented to bleach chambers or special absorbers.

Chlorine gas may also be compressed in reciprocating compressors to either a low pressure (relatively), requiring refrigeration for liquefaction, or higher pressure with moderate cooling.

Nitrosyl Process. A non-electrolytic chlorine process is in successful operation thanks to skillful engineering, and to the relative inexpensiveness of synthetic nitric acid. The overall operation consists of reacting concen-

[33] *Chem. Eng.* (Feb., 1948).
[34] Nash Engineering Co., South Norwalk, Conn.; see sketch in Chapter 31.

trated nitric acid with salt (NaCl) to produce sodium nitrate and chlorine.[35] Nitrosyl chloride, NOCl, is also a product of the first reaction, and it may be utilized with the aid of nitrous acid, itself produced by means of a portion of the nitrosyl chloride. Important reactions are:

$$3NaCl + 4HNO_3 \rightarrow 3NaNO_3 + Cl_2 + NOCl + 2H_2O$$
$$NOCl + H_2O \rightarrow HNO_2 + HCl$$
$$2NOCl + 3HNO_2 + 3O_2 + H_2O \rightarrow 5HNO_3 + Cl_2$$

The nitrosyl chloride, a gas above 22° F. (−5° C.), is also in increasing demand for use as such, and is marketed, in part, as a liquefied gas under pressure.

A second non-electrolytic process for chlorine is a modern version of the Deacon process, in which oxygen (tonnage oxygen), instead of air, with an improved copper chloride catalyst, is employed. Hydrogen chloride is oxidized to chlorine and water at a temperature of 650° C. [1202° F.].

A third process well investigated during the war, involving the action of sulfur trioxide upon salt, and another which rests upon the decomposition of chlorosulfonic acid, have not become established commercially. Both the two latter processes have one of their difficulties in common, the separation of chlorine from an equimolar mixture of sulfur dioxide and itself.[35a]

Shipping Chlorine. The liquid chlorine is shipped in 50- and 100-pound steel cylinders, in single tank car units of 15 or 30 tons, and in 1-ton steel containers of which 15 are placed on a flat car.[36]

The 1-ton unit is very convenient for making the bleach at the pulp or other mill, because the required quantity of milk of lime may be prepared and all the chlorine in the cylinder allowed to pass in without danger of wasting any. Calcium hypochlorite, $Ca(OCl)_2$, and calcium chloride, $CaCl_2$, are formed. All containers have one or two internal pipes, so that either the gas or the liquid may be drawn. If the gas is drawn, heat must be supplied to make up for the heat of vaporization, or else the process is very slow. It is more convenient and simple to use the liquid, mixing it directly with the milk of lime in a small mixing chamber;[37] in that way the process of vaporization uses a part of the heat of reaction of chlorine on lime. In summer, this is important in keeping the temperature of the mixture below 40° C.; above that point the calcium hypochlorite is unstable.[38]

For the chlorination of municipal water supplies, and for any other chlorination away from the manufacturing plant, chlorine in the liquid form

[35] "Is there a profit in chlorine and nitrate from salt?," F. W. de Jahn, *Chem. Met. Eng.*, 42, 537 (1935). U. S. Pat. 2,297,281; 2,261,329; French Pat. 731,320 and addition 44,983; Ger. Pat. 526,476 (1933), 589,072 (1933); Brit. Pat. 398,187.

[35a] "Chlorine production-nonelectrolytic processes," H. F. Johnstone, *Chem. Eng. Progress*, 44, 657 (1948), with 12 sketches and graphs, and 54 references.

[36] Through a decision of the Interstate Commerce Commission the containers are considered as part of the car, and no freight is paid on them. See I. C. C. Docket 13895, 85 I. C. C. 728 (1924); Invest. & Susp. Docket 2456, 104 I. C. C. 196 (Nov. 9, 1925).

[37] U. S. Patent 1,481,106, to James H. MacMahon, assigned to the Mathieson Alkali Works (Inc.), of New York; the time required for the absorption of 1 ton of chlorine is 3 hours.

[38] The bleaching solution used in pulp and paper mills is 6° Bé. and contains 30 grams of available chlorine to the liter.

is preferred. It serves mainly indirectly in the manufacture of a host of chlorine compounds which are essential for the effective prosecution of a war. During World War II, all chlorine production was under Government allocation. Besides helping to maintain healthful water supplies, chlorine is used for fire extinguishers (CCl_4), solvents and degreasing agents, and for bleaching textiles, paper, and many other products.

Distribution of liquid chlorine during a war year is shown in Table 15.

TABLE 15.—*Allocation of chlorine in the war program for the period Jan. 1 to Dec. 31, 1944.**

Total allocations	1,405,340	tons
Export	13,577	
Direct military	37,399	
Other uses	1,354,364	
Chemical manufacture	1,019,187	
Paper processing	166,582	
Metallurgical uses	93,369	
Water treatment	44,504	
Synthetic rubber	5,130	
Food treatment	1,242	
Miscellaneous uses and small orders	23,549	

* "Facts for Industry," March 20, 1947.

Chlorine in car tanks, freight equalized, was listed at $22.50 to $25 a ton (April, 1948).

Gaseous Chlorine and Bleach. Chlorine gas at the generating plant is used, without compression to the liquid, to make "bleach," and for the chlorination of organic substances such as benzene, toluene, pentane, and others.

Bleaching powder is the product of the interaction of chlorine gas and hydrated lime:

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O.$$

The chloride of lime so formed, when dissolved in water, gives equal molecular parts of calcium chloride, which as far as bleaching is concerned, is useless, and calcium hypochlorite, which retains the total bleaching power of the original material

$$2CaOCl_2 \text{ dissolved} \rightarrow CaCl_2 + Ca(OCl)_2.$$

Chloride of lime or "bleach" must not be confused with calcium hypochlorite.

The chlorine absorption is performed either in a series of low-ceiling brick chambers, or in patent shelf absorbers which require little space. In either case the countercurrent principle is applied, the fresh gas meeting the richest bleach; the lean gas, the new hydrated lime. The bleach so prepared has been displaced to a considerable degree (1) by liquid chlorine, in mills and factories, (2) by calcium hypochlorite, $Ca(OCl)_2$, a stable material of high test, whereas ordinary bleach spoils after several months, and has a low test (35 per cent available chlorine). Available chlorine means chlorine evolved on addition of acid; 35 per cent available chlorine is a material which has the effectiveness of 35 parts of liquid chlorine. Pure

calcium hypochlorite, by the laboratory test applied to all bleaching agents, rates 100 per cent available chlorine.[39]

The present quotation for bleaching powder (1948) is $70 a ton, in drums, carload lots.

High Test Hypochlorite [H.T.H.]. Calcium hypochlorite, $Ca(OCl)_2$, essentially free from any other material, in the crystal form, is stable, and efforts to produce it in bulk have been earnest and successful.

One method for its manufacture is the chlorination of a lime slurry followed by the salting out of calcium hypochlorite by means of common salt (NaCl).[40] No organic solvent[41] requiring later recovery is needed. The product may be made essentially 100 per cent $Ca(OCl)_2$, but an additional operation is then required, so that the material actually marketed is 75 per cent $Ca(OCl)_2$. It is therefore twice as strong as ordinary bleach; also it does not spoil on standing, it is not hygroscopic, and when it is made up with water the solution is practically clear.

The latest and most successful method for making high test hypochlorite (H. T. H.) is the formation[42] of the triple salt $Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O$ and its subsequent reaction with calcium chloride. The triple salt is made as follows: 40 parts NaOH, 37 parts $Ca(OH)_2$ and 100 parts water are chlorinated at a temperature below 16° C. (60.8° F.), such as 10° C. (50° F.). This reaction is:

$$(a)\quad 4NaOH + Ca(OH)_2 + 3Cl_2 + 9H_2O \rightarrow Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O + 2NaCl.$$

The comparatively large hexagonal crystals—the triple salt—separate and are centrifuged. In the meantime a special calcium chloride is prepared by chlorinating a milk of lime in these proportions: 74 parts $Ca(OH)_2$, 213 parts water, 71 parts chlorine; the temperature is held at 25° C. (77° F.);

$$(b)\quad 2Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

Next, this solution is cooled to 10° C. (50° F.), the centrifuged crystals are added in the proportion required by the reaction:

$$(c)\quad 2NaOCl + CaCl_2 \rightarrow 2NaCl + Ca(OCl)_2,$$

and the suspension is agitated with paddles. On warming to 16° C. (60.8° F.), reaction (c) takes place and the whole sets to a rigid mass.

[39] The test for available chlorine in bleaching powder consists of acidifying in the presence of potassium iodide. The iodide liberated is titrated. It may be liberated by Cl, but also by oxygen.

Calcium hypochlorite contains 99.7 per cent available chlorine, yet only 50 per cent total chlorine; it is evident that a change in the method of designating the strength of bleaches is desirable. The most logical way would be to state the content of calcium hypochlorite, and this would also be the easiest, for it happens that numerically the "available chlorine" present is almost the same as the calcium hypochlorite content. The chlorine equivalent for calcium hypochlorite is shown by the reactions:

$$Ca(OCl)_2 + H_2SO_4 \rightarrow CaSO_4 + 2HOCl$$

$$2HOCl + 4HI \rightarrow 2H_2O + 4I + 2HCl, \text{ and } 4I \text{ are equivalent to } 4Cl.$$

Bleaching was explained formerly as oxidation; today it would be said to be the taking of electrons. A substance which yields fragments (ions) which take up electrons is an oxidizing agent. Measured in that way, oxygen as well as chlorine is a bleaching agent, a fact already well known in an empirical way.

[40] U. S. Patent 1,754,473 (1930). [41] U. S. Patents 1,481,039-40.

[42] U. S. Patent 1,787,048, to Robert MacMullin and Maurice Taylor; *see also* U. S. Patents 1,787,080, 1,754,474, 1,754,475.

The triple salt $Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O$ becomes $1\frac{1}{2}Ca(OCl)_2 \cdot 2H_2O$. the dihydrate, 2NaCl and water. After drying in the vacuum, a material testing 65 to 70 per cent $Ca(OCl)_2$ results. Such calcium hypochlorite as accompanied the calcium chloride is just that much more product. The NaCl content from (c) is not removed.

There are other high-test hypochlorites of calcium on the market, as for example "Perchloron."

Sodium chlorite,[43] $NaClO_2$, is a new commercial chemical which, combined with chlorine or hypochlorite, gives certain advantages in bleaching paper pulp. It is also finding use in connection with the bleaching and finishing of cotton, rayon and Celanese.

Other Patents

U. S. Patent 1,236,978 on a method for making high test calcium hypochlorite; 1,862,244, on cell construction; 1,862,245, on heat recovery in electrolysis; 1,996,769, manufacture of stable sodium hypochlorite; 2,040,717, 2,028,898, 2,030,694, purifying caustic solutions; 2,031,844, 1,922,591, manufacture of caustic soda; 1,609,757-8, process and apparatus for preparing liquid bleach; 1,944,630 on process for purification of caustic soda solution.

Problems

1. An 18 per cent Na_2CO_3 solution is made to react with a 28 per cent $Ca(OH)_2$ slurry. (a) Assuming the reaction to be complete, what will be the concentration of the resulting decanted caustic soda solution? (b) Consult the curve for conversion against concentration of sodium carbonate solution, and find the figure for 18 per cent Na_2CO_3; using this conversion figure, what will be the concentration of the caustic soda solution? For exact results, the weight of the non-converted Na_2CO_3 present in the caustic soda liquor must be computed and included in the solids which the liquor contains.

2. A batch of soda ash solution containing 19 per cent Na_2CO_3 is treated with the proper amount [use (a) the theoretical, (b) the amount required by a 94 per cent conversion figure] of a milk of lime containing a certain amount of water. How much water must the milk of lime contain, if the resulting caustic liquor is to be 11 per cent NaOH? Find the answer for (a) and (b).

3. A plant causticizes 149 tons of soda ash (98.5 per cent Na_2CO_3) every day. The lime used is 94 per cent CaO. Allowing a 4.5 per cent excess of lime, and assuming that none is recovered, how many tons of lime will be required? What is the production of 50 per cent NaOH liquor, if the yield based on soda ash is 94 per cent?

4. A battery of 60 Nelson cells produces per day 10 tons of chlorine, at an anodic current efficiency of 93 per cent. The cathodic current efficiency is the same. How much caustic soda is produced at the cell? What is the current in ampere hours which passes through the cell if 1 ampere hour is required for 0.00329 pound of NaOH at 100 per cent current efficiency?

5. A plant has 18 tanks with capacity of 40,000 gallons each. The salt solution contained therein is 25 per cent NaCl, and has a specific gravity of 1.200. The plant produces per day 32 tons 850 pounds of 100 per cent NaOH, at 95 per cent yield. What is the storage capacity of the tanks expressed in days? In reality, the final product is 98 per cent NaOH for the diaphragm cell plants, and the remaining 2 per cent is salt (NaCl) and a small amount of carbonate; for the sake of simplicity, the purity is given as 100 per cent NaOH in this problem. Answer: 18 days.

6. The liquor from the electrolytic diaphragm cell contains 12 per cent NaOH and 12 per cent NaCl. For a production of 10 tons of solid caustic per day, how much salt will precipitate in the evaporator, if 2 per cent remains in the caustic? What decomposition efficiency does the cell liquor represent?

[43] "Sodium chlorite, properties and reactions," by M. C. Taylor, J. F. White, G. P. Vincent, and G. L. Cunningham, *Ind. Eng. Chem.*, 32, 899 (1940).

7. Verify the decomposition voltage for salt in solution to produce caustic and chlorine, given as 2.25 in the text. The heat of formation of NaCl is 96,400 gram calories; that of water, 68,370 gram calories, and that of caustic in solution, 112,700 gram calories. Compare Problem 4, Chapter 18.

8. It is desired to manufacture 75 tons of calcium hypochlorite testing 75 per cent "available chlorine" by the salting out method, the first method given under H. T. H. Find out how much lime will have to be used, how much chlorine, and how much calcium chloride in solution will be discarded. The relation may be assumed to be the theoretical ones.

Reading References

"The evaporation of caustic soda to high concentrations by means of diphenyl vapor," W. L. Badger, C. C. Monrad and H. W. Diamond, *Am. Inst. Chem. Eng.*, 24, 56 (1930).

"Hydrochloric acid and sodium sulfate," N. A. Laury, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1927.

"The Principles of Electrochemistry," D. A. MacInnes, New York, Reinhold Publishing Corp., 1939.

"Westvaco sets new record in evaporating electrolytic caustic soda," James E. Lee, *Chem. Met. Eng.*, 37, 404 (1930).

"Chemical plant combines beauty and efficiency," Paul V. Manning, *Chem. Met. Eng.*, 38, 380 (1932), the Hooker electrolytic plant for caustic and chlorine, Tacoma, Wash.

"High test bleaching powder," S. Urano, *Trans. Am. Electrochem. Soc.*, 49, 65 (1926).

"Manufacture of soda with special reference to the ammonia process," Second Edition, T. P. Hou, New York, Reinhold Publishing Corp., 1942.

"Recent advances in causticizing theory and practice," W. E. Piper, *Trans. Am. Inst. Chem. Eng.*, 24, 1 (1930).

"The equilibrium in the causticizing process, Part I," Leo Frank Goodwin, *J. Soc. Chem. Ind.*, 45, 360T (1926).

"Chlorine and salt cake from salt and sulfur," by Arthur W. Hixson and Alvan H. Tenney, *Ind. Eng. Chem.*, 33, 1472 (1941).

"The story of the Hooker cell," by K. E. Stuart, T. L. B. Lyster, and R. L. Murray, *Chem. Met. Eng.*, 45, 354-8 (1938).

"Specific heats of sodium hydroxide solutions," John W. Bertetti and Warren L. McCabe, *Ind. Eng. Chem.*, 28, 375 (1936).

"Settling rate of calcium carbonate in the causticizing of soda ash," by John C. Olsen and Otto G. Direnga, *Ind. Eng. Chem.*, 33, 204 (1941).

"Diaphragm vs. amalgam cells" (for chlorine-caustic production) Robert B. MacMullin, *Chemical Ind.*, 61, 41 (1947).

"New mercury cell makes its bow," W. C. Gardiner, *Chem. Eng.*, 54, 108 (1947).

"Synthetic hydrogen chloride," Aylmer H. Maude, *Chem. Eng. Progress*, 44, 179 (1948).

"Current efficiency studies of the Hooker Type S chlorine cell," R. L. Murray and M. S. Kircher, *J. Electrochemical Soc.*, 86, preprint (1944).

"Caustic purification by liquid-liquid extraction," H. C. Twiehaus and N. J. Ehlers, *Chem. Industries*, 63, 230 (1948).

Atmospheric nitrogen is available in inexhaustible quantities. To convert this vast store of nitrogen into a raw material for the manufacture of indispensable fertilizers and peace-time as well as war-time explosives has been one of the major tasks of the chemist. He has discharged it brilliantly. Of the total compounds made or extracted for their nitrogen values, 75 per cent are "chemical nitrogen," or "air nitrogen" compounds.

Chapter 6

Synthetic Nitrogen Products—The Fixation of Atmospheric Nitrogen—Direct Ammonia, Cyanamide, Nitric Acid from Ammonia by Contact Catalysis

As long ago as 1780 Cavendish caused the combination of the nitrogen and oxygen in the air by means of an electric spark. The first practical large-scale manufacture of a nitrogen compound from atmospheric nitrogen was that of Birkeland and Eyde, at Nottoden, Norway, early in this century. In this process air is passed at a rapid rate through an arc spread out to form a flame. A previous attempt by Bradley and Lovejoy at Niagara Falls in 1902, using the arc method, had failed because the arc flame area was too small and because the gases were not removed from the reaction chamber fast enough. The Norwegian process benefited from the demonstrated faults in this installation.

The manufacture of synthetic ammonia was tried a little later, and succeeded first in the Haber process, in which a mixture of nitrogen and hydrogen is passed at moderately high temperature and under pressure over a contact catalyst, which causes a partial conversion of the elemental gases into ammonia. Several modifications of the process have been developed for making ammonia from the elements; they have been so successful that this process is now more important than all other synthetic processes combined. Ammonia salts are valuable fertilizers; moreover, if nitric acid is called for, ammonia may be oxidized with atmospheric oxygen by the aid of a contact catalyst, so that the synthetic ammonia process may also produce from atmospheric nitrogen, in an indirect way, what the arc process furnishes directly.

An entirely different process for the fixation of atmospheric nitrogen is the calcium cyanamide process, which depends upon the fact that metallic carbides, particularly calcium carbide, readily absorb nitrogen gas to form the solid cyanamide. This substance as such is a fertilizer. By a further treatment it may be transformed into cyanide, by another into ammonia; but this ammonia is more costly than direct synthetic ammonia. The process was developed by Frank and Caro in Germany, in 1895-97, and has been introduced in many countries since that time, among others in the United States and Canada.

Another proposed process for binding the nitrogen gas of the air in the form of a chemical compound easily transported, which is what "fixation of atmospheric nitrogen" means, was the Bucher process which was intended

to produce cyanides, ferrocyanides, or hydrocyanic acid without using a carbide. It is of no commercial importance at present.

Finally, nitrogen may be passed over metals at suitable temperatures to form nitrides which on treatment with steam yield ammonia. The best known process which embodies this principle is the Serpek process, manufacturing aluminum nitride; it has been introduced in France but not in America.

The various processes with actual or potential values for the fixation of atmospheric nitrogen may be grouped together as follows:

a. The various arc processes in which ordinary air is passed at a rapid rate through a broad or long arc. The products are nitrates, nitrites, or nitric acid. This was the earliest method, but is hardly a factor any more.

A thermal process for the synthesis of NO from the atmosphere has reached pilot plant stage and is promising.

b. The direct synthetic ammonia process, requiring nitrogen free from impurities, and pure hydrogen. The two gases mixed sweep over a catalyst while under pressure and at an elevated temperature; the product is ammonia, which may be further combined as a salt, such as the phosphate, the nitrate or the sulfate. By catalytic oxidation, the ammonia may be changed to nitric acid, and this in turn into nitrates. The great expenditure of electrical energy required in *a* is avoided in *b*.

c. The cyanamide process, which also requires fairly pure nitrogen, as well as calcium carbide, itself a product of the electric furnace. The material produced is calcium cyanamide. By steaming in autoclaves, ammonia could be produced, but this is rarely done.

Only the direct synthetic ammonia process and the calcium cyanamide process are of industrial importance today, and the former surpasses the latter.

d. The cyanide and ferrocyanide processes, in which nitrogen is passed into a vessel containing an alkali and coal mixed and heated.

e. The nitride process, in which nitrogen gas unites with certain metals. The product is treated with water, yielding ammonia.

The reason why the fixation of atmospheric nitrogen has been a difficult task is that elemental nitrogen is comparatively unreactive. It combines with only a few other elements, and then only by violent means, such as elevated temperatures.

The capacity for the production of direct synthetic ammonia in the United States, on January 1934, was 341,350 tons (2,000 lbs.) of nitrogen annually, which was 10.6 per cent of total capacity of similar plants for the world. Germany was the leader, with 1,136,080 tons installed capacity.[1] In 1949, the United States installed capacity,[5] private and government-owned, is 1,644,000 short tons. Since 1941, the annual U. S. production of synthetic anhydrous ammonia has exceeded 500,000 short tons of NH_3. In 1945, the U. S. production for all known private commercial manufacturers of anhydrous ammonia was 548,655 tons; in 1946, it was 725,537 tons; in 1947, 1,117,212 tons.

[1] A richer table will be found in "Chemical Nitrogen," Report 114, *U. S. Tariff Commission* (1937), tables 7 and 70. An earlier article is "World nitrogen developments in 1931," Chapin Tyler, *Chem. Met. Eng.*, 39, 44 (1932).

The world production of nitrogen from all sources is given in Table 16.

TABLE 16.—*World production of nitrogen including by-product chemical nitrogen during the year ended June 30, 1947.**

	000 metric tons
Europe	1208.5
Asia	197
Africa	18
Oceania	6.5
America	1410
Total	2840

* Bureau of Plant Industry, Soils, and Agricultural Engineering, Dept. of Agriculture. The figure for Europe includes all Germany, but not U.S.S.R.

The consumption by countries is shown in Table 17.

TABLE 17.—*World consumption of nitrogen by countries, in the year ended June, 1947.*†

	000 metric tons		000 metric tons
Belgium	90	Other Asia	17.5
France	201	Egypt	49.5
Holland	96	Other Africa	29.5
Norway	23.5	Oceania	17
United Kingdom	218	U. S. A.	978.5
Other Europe	710	Canada	33
China	55	Chile	9.5
India	39.5	B. W. Indies	5
Ceylon	8.5	Other American	28
Japan	221	Total	2830

† Bureau of Plant Industry, Soils, and Agricultural Engineering, Dept. of Agriculture.

Eighty-four per cent of the total world consumption was in the form of fertilizer.

Table 18 was compiled during pre-war years, but it still has value, inasmuch as the nitrogen compounds are listed by processes.

TABLE 18.—*World production of inorganic nitrogenous materials.*

	Quantity produced during the year ended June 30 Expressed in short tons of Nitrogen*	
	1937	1938
Sulfate of ammonia		
By-product	472,900	453,000
Synthetic	758,400	843,300
Cyanamide	320,800	336,200
Nitrate of lime	197,300	214,900
Other forms of synthetic nitrogen†	938,100	1,026,200
Other forms of by-product nitrogen	58,400	54,000
Chilean nitrate of soda	227,100	246,900
Total world production	2,973,000	3,174,500

* Bureau of Chemistry and Soils, compiled from the British Sulphate of Ammonia Federation, Ltd., annual report. Fertilizers are included in this table under the final form as sold; for example, cyanamide, if converted into sulfate of ammonia, is included under "synthetic sulfate of ammonia," or, if into Ammophos, under "other synthetic nitrogen."

† Other forms of synthetic nitrogen mean: anhydrous liquid ammonia, Nitrochalk, Calnitro, urea, sodium nitrate, Ammophos, and others.

For the year 1935-36, the synthetic nitrogen products were 75.1 per cent, the by-product nitrogen compounds 17.3 per cent, and the Chilean nitrate 7.6 per cent of the total world production. For 1937-38, the corresponding figures were 76.1, 16.1, 7.8 per cent.

The world production capacity for synthetic nitrogen in 1936 was 3,700,000 tons a year. It is nearly 5,500,000 tons today (1948).

No data are available for subsequent years.

The Electric Arc Process, Using Air

The electric arc has been successfully applied to the fixation of atmospheric nitrogen; it was the first method evolved which permitted the fixation of such nitrogen. The main developments were the Birkeland and Eyde, in Norway; the Schoenherr, in Germany, and the H. and A. Pauling in Austria; in each of these developments, the shape of the arc differs, and also the shape of the furnace. They agree, however, in the nature of the reaction, the union of atmospheric oxygen and nitrogen to form nitrogen oxide, NO, under the influence (chiefly thermal) of the arc; in all three, the reacted air, with 1 per cent NO, must be withdrawn from the reaction zone as rapidly as possible, to prevent decomposition. This first oxide is oxidized further and absorbed in water or in lime, to give nitric acid of medium concentration in the first case, or calcium nitrate, a fertilizer, in the second case. Since the advent of synthetic ammonia, these furnaces have lost their importance. One other reason for their failure is the high power requirement; 1 kilowatt year was required for the production of 600 kilos of nitric acid calculated as 100 per cent HNO_3.[2]

The temperature of the flaming arc was estimated as 3200° C. (6000° F.).

In the new thermal process for nitric oxide, preheated air strikes a bed of hot refractory pebbles offering 22 sq. ft. of surface for each cubic foot of volume. In its tortuous path past the pebbles the air acquires turbulent flow; its temperature becomes high enough to form nitric oxide. Quick cooling, necessary if the nitric oxide formed is to be preserved, from a high of 4200° F. (2315° C.) to below 2800° F. (1536° C.) is achieved by passing the gases through another bed of refractory pebbles which are cold. A concentration of 1.75 per cent NO results; after further cooling, the gas is oxidized further and absorbed in water, or in alkali to form nitrates. The pebbles are heated by direct impact of an oil flame; the fire gases leave with the air mixture. Zirconia pebbles with the highest melting point hitherto commercially attainable, are used in the furnace, which has twin units.[3]

The Direct Synthetic Ammonia Process, by Catalysis

If nitrogen and hydrogen are mixed and brought in contact with a substance such as specially prepared porous iron granules, at elevated temperature and under high pressure, they unite to form ammonia:

$$N_2+3H_2 \rightarrow 2NH_3+24 \text{ Cal.}$$

Even without the contact substances, the two original gases form ammonia in minute amount; this is of extreme importance, for a catalyst can only hasten the reaction which takes place to a slight extent without it. That an increase in pressure should favor the formation of ammonia is due to the fact that 4 volumes of the original gases are changed into 2 volumes of the

[2] "The fixation of atmospheric nitrogen," Joseph Knox, New York, D. Van Nostrand Co., 1914. *See also* first edition of the present book.

[3] *Chem. Ind.*, 58, 245 (1946); see also U. S. Pat. 2,421,744 to Farrington Daniels, and 2,422,081 to F. G. Cottrell; Can. Pat. 433,314, Feb. 26, 1946.

final gas.[4] The temperature must be just high enough to allow high activity: beyond a certain value, an increase in the temperature retards the reaction by favoring the decomposition of ammonia. The amount of ammonia expressed in percentage by volume, for different pressures and temperatures, in the presence of a catalyst, is shown in Table 19.

TABLE 19.—*Percentage ammonia at equilibrium.**

Ratio $H_2/N_2 = 3$.

Temp. °C.	Pressure (atm. absolute)						
	1	10	50	100	300	600	1000
200	15.30	50.66	74.38	81.54	89.94	95.37	98.29
300	2.18	14.73	39.41	52.04	70.96	84.21	92.55
350	0.90	7.41	25.23	37.35	59.12	75.62	87.46
400	0.44	3.85	15.27	25.12	47.00	65.20	79.82
500	....	1.21	5.56	10.61	26.44	42.15	57.47
600	....	0.49	2.25	4.52	13.77	23.10	31.43
700	....	....	1.05	2.18	7.28	....	12.87

* Compiled from publications of the Fixed Nitrogen Research Laboratory by Dr. Alfred T. Larson.

These values are obtained only if plenty of time is available, more time than can be allowed in a commercial application. A moderate percentage,

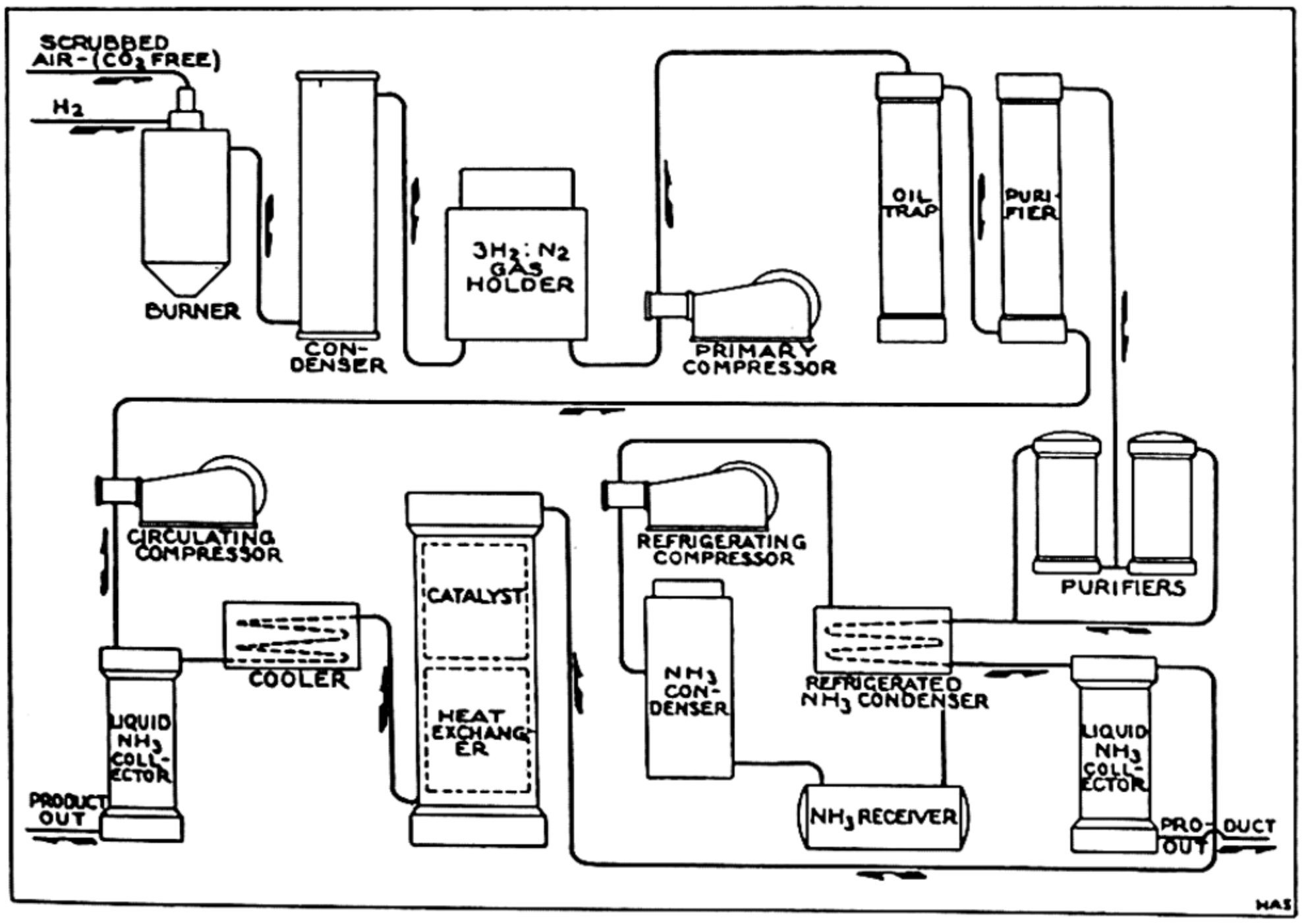


FIGURE 45.—Flow sheet for the direct synthetic ammonia process. The catalyst chamber and heat exchanger are combined in one tower about 40 feet high. On leaving the heat exchanger the gas deposits about half its ammonia content in the cooler at left of figure; the residual gas with its ammonia content is recirculated, and loses much of its ammonia in the refrigerated ammonia condenser at right of sketch. The recirculated gas is several times the make-up. (Drawn and reproduced by courtesy of Mathieson Chemical Corp., N. Y.)

[4] This is in conformity with the principle of Le Chatelier, that "if an outside impulse is applied to any system in equilibrium, the system tends to rearrange itself to absorb that impulse." In this case, the gases contract, in obedience to the pressure applied, by changing, to a greater extent, to the less voluminous ammonia.

but one quickly reached, is best suited to a commercial development, and the rapidity depends upon the nature of the catalyst. All the gases do not react, but that is not necessary to render the reaction of commercial value; if the portion which has reacted is about 5 per cent, it can be removed and the remaining gases used over again. Several systems depend upon this principle: the Haber in Germany, the Claude in France, the Casale in Italy, and the American in the United States.[5] The Haber was the first to employ the direct synthetic method, and the others are indebted to it for the demonstration of the feasibility of the process on a commercial scale. The Claude, the Casale, and the American (or F. N. R. L.) systems are, however, independent developments of the general principle common to all four. They differ from the Haber and from each other in the pressure employed, in the method of removing the ammonia formed, and in the preliminary manufacture and purification of the raw gases. Additional processes with characteristic features are the Fauser, and Mont Cenis.

The American system is the contribution of the Fixed Nitrogen Research Laboratory, U. S. Department of Agriculture, Washington, D. C. The details of this system have been made public without reservation, including the method of preparing the catalyst; it will therefore be presented first.

The American System. The method for the preparation of a mixture of 3 volumes of hydrogen and 1 volume of nitrogen differs with the size of the plant as well as with the system operated. In a small-scale installation, for experimental purposes, a simple way is to burn hydrogen from electrolytic cells which decompose water, in insufficient air. The oxygen of the air is fixed as water and this is removed by a cold-water condenser; the gas passing out of the condenser will consist of hydrogen excess, mixed with nitrogen. For full-scale installations, a mixed water gas, producer gas, and steam is passed over suitable catalysts; the carbon monoxide reacts with steam to form carbon dioxide and hydrogen. The carbon dioxide is scrubbed out as described more fully under the Haber process. Hydrogen from any source (Chapter 19) and nitrogen from the liquefaction of air may be mixed in the proper proportions and used.

Natural gas and water gas were the two main sources of hydrogen for the ten new wartime synthetic ammonia plants; six of the ten used natural gas (catalytically reacted with steam); four used water gas based on coke. The several other processes for hydrogen produced, in many small plants, a minor quantity of hydrogen for the synthesis. During wartime, the hydrogen production facilities were increased to about 9 billion cubic feet per month, three times the pre-war figure.[5a] Currently about 3.2 billion cubic feet of hydrogen per month are produced and consumed in ammonia synthesis.

[5] The actual production for 1939-40 in the United States is reported fo have been 245,000 tons of nitrogen (Soil and Fertilizer Investigations, Bureau of Plant Industry, U. S. Department of Agriculture); with the construction of two new plants, one at West Henderson, Ky., the other at Morgantown, W. Va., the total capacity for direct synthetic ammonia was well over 400,000 tons of nitrogen a year in 1942. Over the period of World War II, additional facilities were developed, so that at this time (November, 1948) the installed capacity is in the neighborhood of 1,200,000 tons of N a year, under private control, with an additional 409,000 tons under government operation.

[5a] *Trans. Am. Inst. Chem. Eng.*, **42**, 380 (1946).

The Purifier. The several steps in the American system are illustrated in the flow sheet on page 115. The hydrogen was obtained in this case from electrolytic cells, because of their compactness and ease of operation. A blower feeds the hydrogen to the burner; a cold-water condenser liquefies the water formed and a trap removes it. A compressor (4-stage) delivers it at a pressure of 300 atmospheres to the purifier, which is really a low-efficiency converter. (*See* Fig. 46.) A small amount of ammonia is formed,

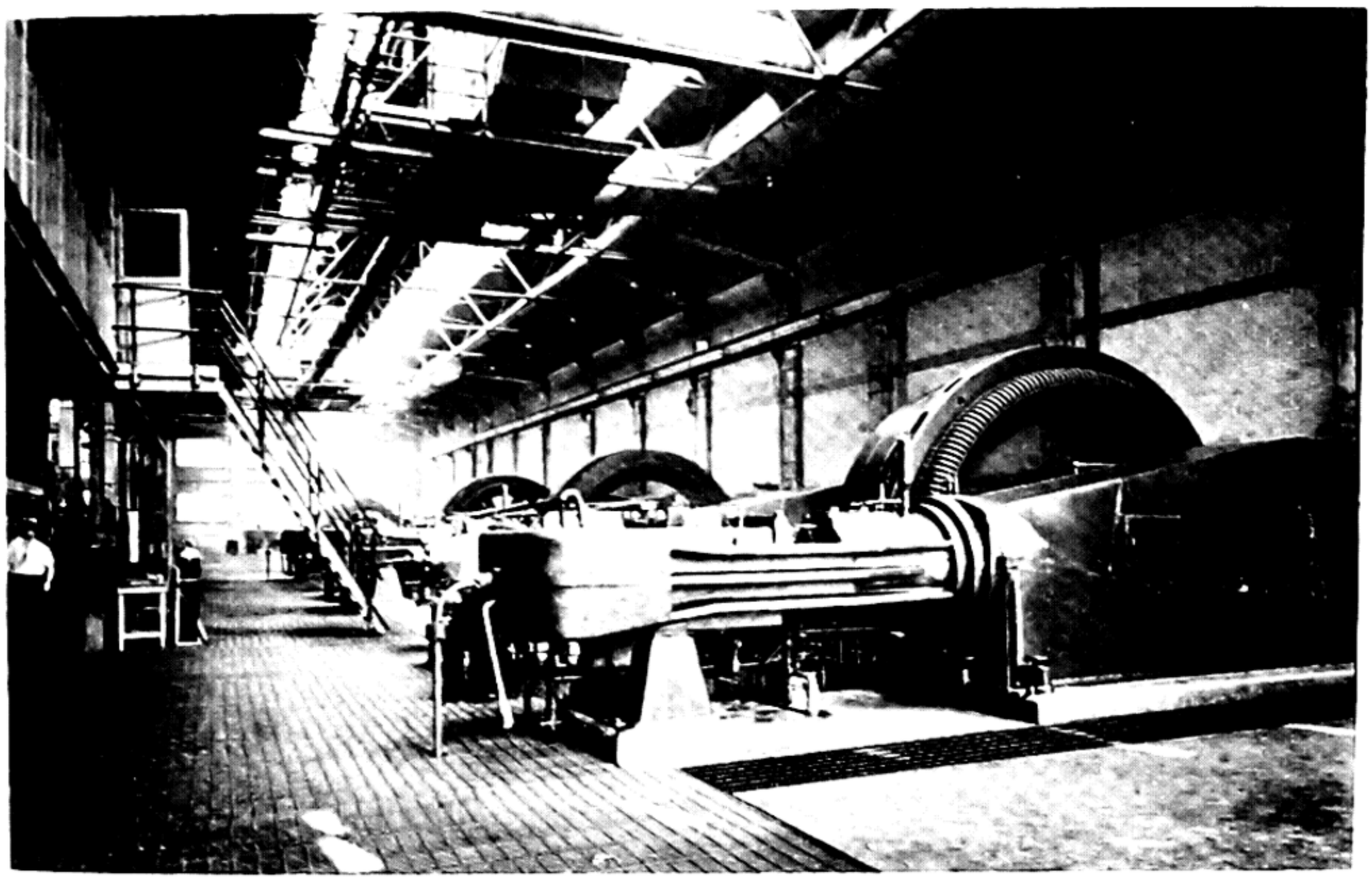


FIGURE 46.—Hypercompressors for direct ammonia synthesis, Belle works, Charleston, W. Va. Each delivers compressed nitrogen plus hydrogen gas at the pressure of 7½ tons per square inch. (Courtesy of E. I. du Pont de Nemours & Co., Inc., Ammonia Department, Wilmington, Del.)

and condensed to the liquid state in the cold water condenser immediately following it. This condensed ammonia retains all impurities which the contact substance itself does not fix, so that the gas issuing from the condenser and separator is of the required purity. This gas is now fed to the high-efficiency converter, where the main conversion takes place; its contact material is maintained at a temperature of 475° C. (887° F.).

The Catalyst. The heart of the process is the converter, and the essential part of the latter is the contact substance. For the American system, exact knowledge of its nature is available.[6] The high-efficiency catalyst consists of iron oxide granules containing the "combined promoters," potassium and aluminum oxides; the proportions are approximately 1 per cent potassium oxide and 3 per cent aluminum oxide, based on the weight of iron oxide. The preparation of the catalyst is as follows:[7] Iron oxide, which may be prepared by burning pure iron in oxygen, is fused in an

[6] U. S. Patent 1,489,497 to Alfred T. Larson.
[7] U. S. Patent 1,554,008; or *Ind. Eng. Chem.*, 17, 971 (1925).

electric furnace; to prevent contamination, the hearth of the furnace is made of natural magnetite; the combined promoters are added to the fused mass, in the proportion given above. After the furnace has cooled, the oxide catalyst is removed, crushed, and sieved to give granules of uniform size. These are placed in the converter; the first portions of hydrogen gas in the regular mixture of nitrogen and hydrogen reduce the iron oxide to the metal; during this reduction, the granules probably become porous, which means the development of considerable surface. The explanation of the beneficent effect of the promoters is that they prevent sintering, and hence preserve the porosity.

The life of the catalyst is about 100 days, after which it must be replaced; raising the temperature to 500° C. (932° F.) greatly shortens the life of the catalyst mass.

The Converter. The converter for a 3-ton plant is an upright cylinder of chrome-vanadium steel 21 inches in diameter widening to 24 inches near the top which carries the removable head; the height of the cylinder is 7 feet. It is made of a single forging except for the head, which is held in place by nickel-steel bolts. The walls are 3 inches thick. For greater capacities, the dimensions are correspondingly larger (see under Claude process). The compressed gas enters the converter at the base and leaves at the top. The converter contains not only the contact substance but also the heat interchanger. In the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, heat is evolved; as much as possible of that heat is transferred to the incoming cold gases, so that the temperature at which the reaction is to take place may be attained without expenditure of fuel. This is not quite realized, and some supplementary heat must be supplied by means of a coil of resistance wire electrically heated and placed at the base of the interchanger, heating the gas as it enters the contact mass.

The interchanger is placed in the center of the converter, running through the whole height; around it is the contact mass, distributed in three concentric chambers of unequal sizes. A first narrow chamber surrounds the interchanger; a second, somewhat wider, chamber surrounds the first; the third similar chamber is the widest. The new gases first pass through the interchangers, to be heated. On leaving the central interchanger, the gas passes up the first chamber, down the second, and up the third, then down one coil of the interchanger and up the other to the outlet in the head of the converter. These various passages and the construction are shown in Figure 47. Each coil of the heat interchanger is double; through the central coil the cold gas flows; through the outer one the hot gas; no communication between the two gases is possible. The several contact chambers are formed by steel tubes.

The third chamber leaves a narrow passage between itself and the outer wall of the converter shell. It is through this space that the cold gas, which has entered at the bottom, streams on its way to the channels leading to the inner coil of the interchanger; this incoming cold gas keeps the shell relatively cool and therefore better able to resist stresses.

From the converter the gas enters the first condenser, which is water-cooled, where a part of the ammonia is liquefied. It then enters the circu-

lating pump, lubricated by the liquefied ammonia in the gas. In the main condenser which follows, the cooling is by expanding ammonia, and here all the ammonia in the gas is liquefied. It is collected in receivers and pumped out of these by a liquor line. The receivers act at the same time as separators, the uncondensed gas passing out through a line which brings it to the converter entry. Mixed with fresh gas from the compressor, it undergoes partial conversion anew.

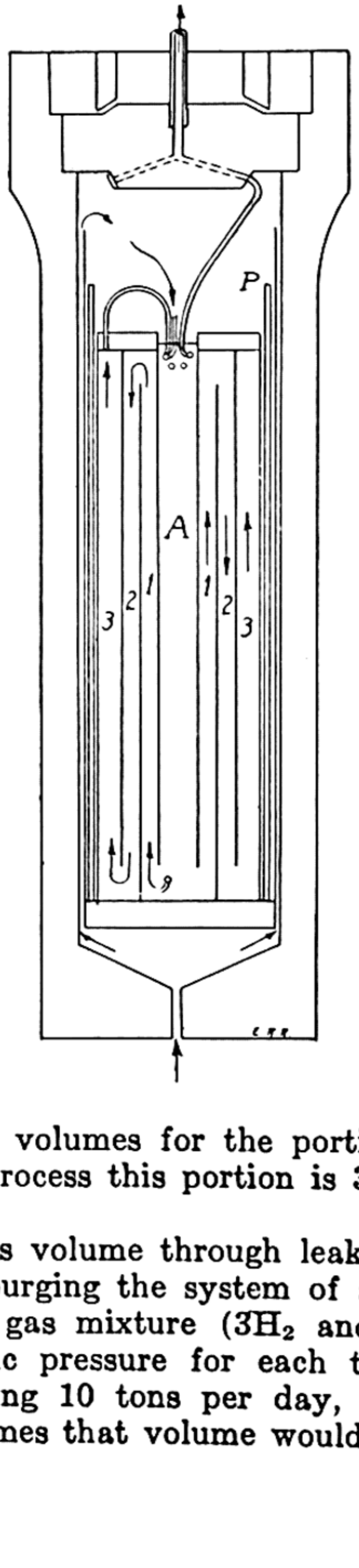


FIGURE 47.—Converter for the American system for ammonia. *A*, space for the two double-walled coils of the heat exchanger; 1, first contact chamber in which the gas travels upward; 2, second chamber, with downward travel; 3, third chamber with upward travel. *P*, "Pyrex" glass reflector.

There is contraction from 4 volumes to 2 volumes for the portion of the gas which has reacted; in the American process this portion is 30 per cent.

If there is a loss of 10 per cent of the gas volume through leaks and through the loss of unconverted gases when purging the system of argon, there are required 100,000 cubic feet of the gas mixture ($3H_2$ and N_2) measured at 20° C. (68° F.) and atmospheric pressure for each ton of ammonia manufactured. In a plant producing 10 tons per day, which would still be a plant of moderate size, ten times that volume would have to be handled.

The product is obtained in the form of anhydrous ammonia of high purity; it is therefore ready for use in refrigerating plants using ammonia as working medium. In former days a special process was required to change the aqua ammonia made from the gas works liquor into the anhydrous liquid ammonia in steel cylinders. At one time, it was difficult to sell the ammonia from gas liquor for 30 cents a pound, anhydrous, and make a profit; now anhydrous ammonia is quoted at 5 cents (in tank cars). The market for such anhydrous ammonia is limited, and it is therefore invading the fertilizer market in the form of sulfate of ammonia. A tremendous market is opened, now that the ammonia is oxidized to nitric acid from which calcium nitrate and sodium nitrate are made, decreasing still further the importance of the Chilean deposits. The oxidation of ammonia to nitric acid is described at the end of this chapter.

The Haber Process. The catalyst in this system is promoted iron; the pressure is 200 atmospheres, and the temperature 550° C. (1022° F.). The conversion is comparatively low, about 8 per cent. The process is a complete success, nevertheless. The same company which developed the contact process for sulfuric acid, the Badische Anilin und Soda Fabrik, is also the company which fathered the Haber process; it is now (1937) part of the Interesse Gemeinschaft Farbenindustrie (I. G.), a huge combination of German chemical plants, with an installed capacity of over one million metric tons of nitrogen per year.

While the catalytic conversion is credited to Dr. Haber, the important problem of providing the raw gases cheaply and in the huge volumes required was solved by Dr. C. Bosch. Water gas,[8] made by blowing steam over glowing coal or coke, and consisting essentially of equal volumes of hydrogen and carbon monoxide, is mixed with producer gas[8]; the latter consists essentially of nitrogen, two parts, and carbon monoxide, one part. The mixed gases are mixed still further with steam, and this new mixture is sent through a hot catalyst which causes the water to react with the carbon monoxide to form hydrogen and carbon dioxide; the nitrogen remains unaffected (*see* Fig. 48). The catalyst used in this case is iron oxide containing small amounts of chromium and cerium. The proper volumes are chosen to give at this stage hydrogen and nitrogen in the ratio by volume of three to one; but there is present the undesirable carbon dioxide and some carbon monoxide which has escaped the action of the steam. In order to remove carbon dioxide, the gases are put under pressure (50 atmospheres) and scrubbed with water, which at such pressures dissolves carbon dioxide readily; some remains, and is scrubbed out with a solution of caustic soda. The carbon monoxide is removed by scrubbing in ammoniacal copper formate while under 200 atmospheres pressure, which is the working pressure for the catalytic conversion. The cost of the gas mixture by this method is low, so that in the absence of hydrogen as a by-product it will probably be generally adopted.

The converter[9] is similar in principle to the one described under the American system. The proportion of the ammonia in the gas issuing from

[8] Chapter 15.
[9] U. S. Patent 1,202,995.

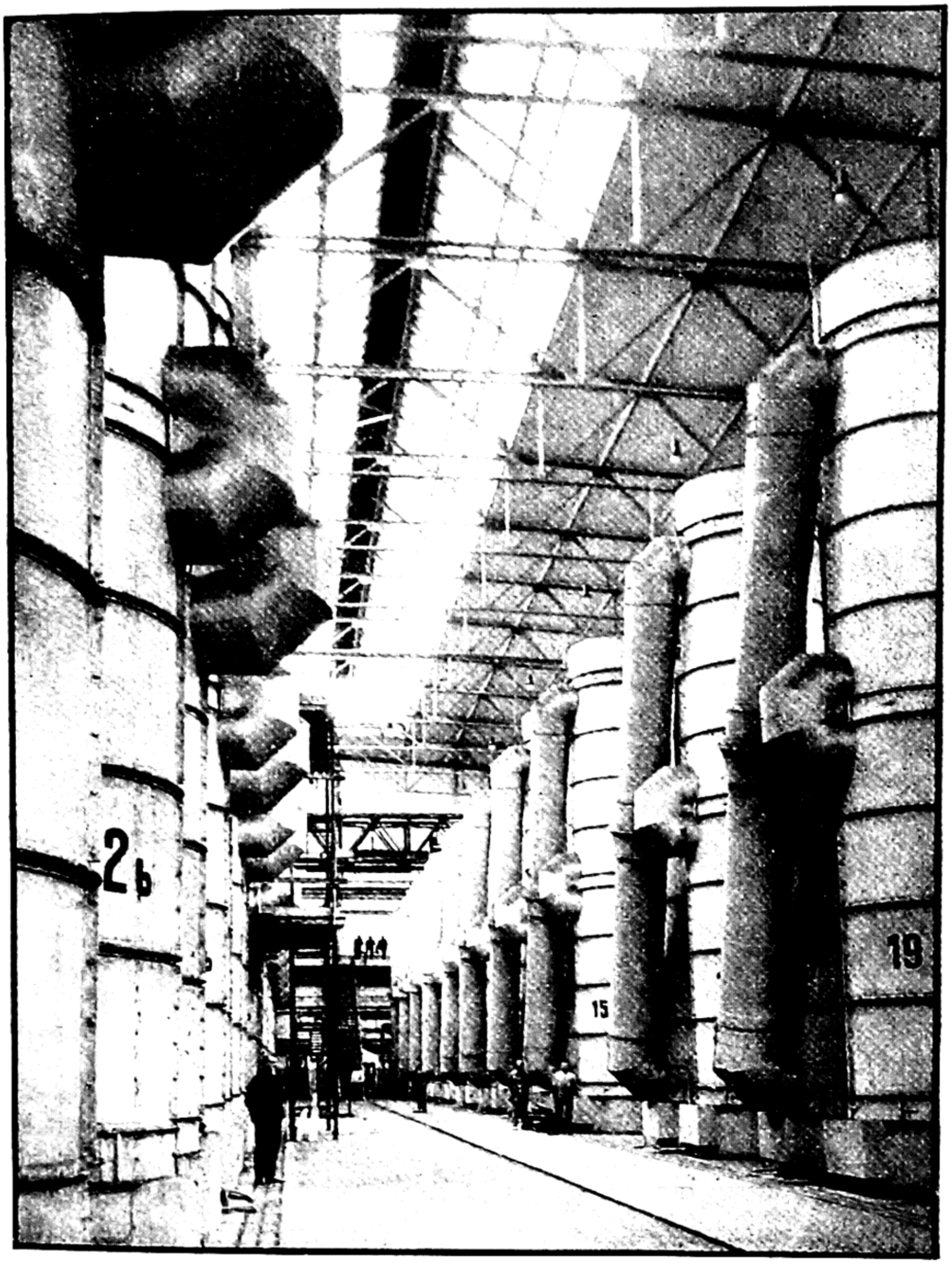


FIGURE 48.—Catalytic conversion of carbon monoxide to the dioxide by interaction with steam in the production of hydrogen for the ammonia synthesis, at the Leuna works of the I. G. Farbenindustrie. Each unit consists of a pre-heater, the lower section, and the reaction chamber above it. In the course of World War II, the plant was damaged, but it continued to function to 20 per cent of capacity. Presumably it is in operation at the present time. (Bourke-White Photo, from Pictures, Inc., Chrysler Building, New York.)

the converter is so low that mere cooling does not liquefy it sufficiently, and it must be removed by solution in water. The unconverted gases are freed from moisture and circulated through the converter with fresh gas, for further conversion. The ammonia water, which is the primary product, may be made to give up its ammonia gas very simply by means of continuously operating stills, or in stripping towers, described in Chapter 1, Part I.

The Mont Cenis Process.[10] Similar to the Haber, and of more recent development, is the Mont Cenis direct ammonia process. Use is made of a highly active catalyst (an iron-cyanide complex), which is effective at the comparatively low pressure of 100 atmospheres, and at the temperature of 400° C. (752° F.). The ammonia is obtained in liquid form at once.

The Claude System. The Claude system is distinguished by the high pressure used, higher than either the American (in the original form) or the Haber, namely, 900 atmospheres. The source of its hydrogen is coke-oven gas. There is present in coke-oven gas not far from 50 per cent hydrogen; removing it causes an increase in the B.t.u. value of the residual gas.

The hydrogen is separated from the other constituents by refrigeration. At the temperature of liquid air (— 180° C. or — 292° F.), only hydrogen remains a gas; it contains some methane and carbon monoxide which escape liquefaction. The nitrogen is obtained from liquid air;[11] it is mixed with the impure hydrogen; the two are compressed to 900 atmospheres in an eight-stage compressor, and passed through a purifier containing a catalyst which changes the carbon monoxide, at the expense of some hydrogen, to methane and water. The water is removed, but not the methane, for it is harmless to the ammonia catalyst. The hydrogen-nitrogen mixture with its methane content enters a series of four converters; in each some ammonia is formed, which is removed by cooling before the gas enters the next converter. Issuing from the last converter, the unconverted gas contains 10 per cent of methane; all this gas is returned to the original hydrogen separator which produced the first slightly impure hydrogen. From this separator the methane, mixed with carbon monoxide, is removed in the liquid state, and after gasification is burned under boilers. The portion of the gas mixture (H_2 and N_2) converted in the four converters is 80 to 85 per cent. There is no recirculation of the gas as in the American system.

To withstand the high pressure accompanied by the high temperature, which varies between 500° and 650° C. (932° and 1202° F.), a special alloy is used: for example, 60 per cent nickel, 25 per cent chromium, 0.6 per cent carbon, the rest iron; or nickel 60.4 per cent, chromium 8.7 per cent, tungsten 2.5 per cent, carbon 0.4 per cent, and iron 25 per cent. The high temperature means that the catalyst loses its activity rapidly; the active mass must be replaced every 10 or 12 days. The change is made in 5 hours, thanks to the simple construction of the converter.

As advantages possessed by the Claude process may be listed: the handling of more material in a given reaction space compared with processes using lower pressures; a high space-time yield, made possible by the high temperature which favors rapidity of reaction (*see* Table 20); the fact that

[10] *Proc. Intern. Conf. Bituminous Coal, 2nd Conf.,* Pittsburgh, Pa., 2, 202 (1928).

[11] Chapter 19.

as the activity in the first converter drops somewhat, the second converter functions to a correspondingly higher degree, so that the over-all activity does not fall off.

With converters 27.5 inches in diameter and 11.5 feet high, 30 tons are made per day (900 pounds pressure); with converter tubes 39.37 inches outside diameter and 13.5 feet high, 50 to 100 tons may be produced. These sizes may be compared to Haber converters, 20 feet high and 4 feet outside diameter with 7-inch walls.

The Casale System. The original development under this system required a pressure of 750 atmospheres, and this has been raised still further. One converter is used,[12] and the gas is recirculated frequently. An important advantage of working at such high pressures is that water cooling is sufficient to remove the ammonia formed; another, perhaps more important, is the high conversion obtained—40 per cent in a single passage through the converter. Except for the high pressure, this system resembles most the American system.

In 1934, there were 24 Casale plants in operation, of which 10 were in France. Of the 24, 9 were run on hydrogen from coke-oven gas, 10 on electrolytic hydrogen, 3 on water gas hydrogen.

The Fauser Process.[13] This process makes use of the oxidation of a portion of its ammonia in order to furnish its nitrogen for the direct ammonia synthesis. Ten per cent of the ammonia manufactured is mixed with air and passed to a platinum gauze converter. The oxides of nitrogen are scrubbed out and the residual gas saved. It consists mainly of nitrogen, but with a small amount of oxygen. It is mixed with hydrogen and passed over platinized asbestos, so that all the oxygen is changed to water. This latter is removed by cooling, and the purified gas is now pure nitrogen and hydrogen.

Table 20 permits comparison at a glance of the various systems for the direct synthesis of ammonia from the elements:

TABLE 20.—*Comparison of synthetic ammonia processes.*

	Pressure atm.	Reported temperature °C.	Reported conversion maximum Per cent	Recirculation of unchanged gases	Catalyst
American	300	475	30	yes	Iron granules, promoted
Haber	200	550	8	yes	Iron granules, promoted
Claude	900	600	40	no	Iron granules, promoted
Casale	750	475	40	yes	Iron granules, promoted
Mont Cenis	100	400	40	yes	Iron-cyanide complex

The plants in the United States follow essentially the American process, or a modification of it. It may be estimated that 50 per cent of the world production of nitrogen compounds is by the American process for ammonia (1948).

The preliminary work included a study of the content of ammonia in a mixture of hydrogen and nitrogen in contact with a catalyst at equilibrium.

[12] U. S. Patents 1,408,987 and 1,447,123, both with drawings showing construction of the converter.

[13] A flow-sheet for the Fauser ammonia system will be found in *Chem. Met. Eng.*, 38, 628 (1931).

But it must be remembered that in practice the figure for ammonia formation attainable at equilibrium is not reached, because the gases are not allowed enough time in contact with the catalyst; the conversion must take place rapidly, for the gases stream by at a rapid rate.

To make comparisons between runs at different pressures and rapidity of flow, the concept of space velocity is used. Space velocity is the number of liters of exit gas, corrected to 0° C. (32° F.) and atmospheric pressure, which pass over 1 liter of catalyst mass per hour. The space velocity for the direct ammonia processes is 40,000 on an average, with variations at the several plants.

Space-time yield is another useful value; it is the yield of ammonia per liter of catalyst per second.

It should be remembered also that as the pressure is increased, the volume of the reacting gases becomes smaller, so that a comparatively small catalyst bomb will handle a considerable volume of free gas. (See problems at the end of the chapter.)

A number of further statements regarding catalysis will be found in Chapter 25.

Shipments. Liquid anhydrous ammonia is transported in steel tanks of various sizes, the standard capacity being 50,000 pounds in a single unit. It is also shipped in steel cylinders containing 25, 50, 100, and 150 pounds of ammonia.

Uses. The main use for ammonia is for fertilizer manufacture, chiefly in the form of ammonium sulfate, or as ammonium nitrate, phosphate, or as urea. It serves as raw material for manufacturing nitric acid which, transformed into sodium or calcium nitrate, also finds its way into fertilizers. A table on the nitrogen industry process-product relationships for the world will be found in Report 114, U. S. Tariff Commission, 1937.

Ammonia serves the many uses to which an alkali may be put. Anhydrous ammonia is the most important refrigerating agent, because of its low cost and high thermodynamic efficiency. Ammonia is coming into use as a water purification agent, and as a nitriding agent for steel. It is an important material in synthetic organic products, such as synthetic urea.

A rather novel use for ammonia is as a source of hydrogen, by passing anhydrous ammonia gas at atmospheric pressure over a catalyst heated to about 600° C. (1112° F.), such as an incandescent "Nichrome" wire coil. The great advantage lies in the fact that a 100-pound ammonia cylinder, easily transported, yields 3400 cubic feet of hydrogen (mixed with 25 per cent nitrogen).[14]

The Cyanamide Process. In the cyanamide process, ground calcium carbide[15] is placed in iron drums each holding a charge of 4000 pounds, and fitted with a pipe connection so that nitrogen may be fed in. The center of the charge is heated by means of an electrically heated carbon rod and the nitrogen turned on; it is absorbed by the hot carbide, and the reaction evolves so much heat that the carbon rod may be removed after a few

[14] "Ammonia as a source of hydrogen and nitrogen," J. F. T. Berliner and G. W. Burke, *Trans. Am. Inst. Chem. Eng.*, 25, 42 (1930).

[15] Chapter 17.

minutes; the heat of reaction is sufficient to keep the mass at the reaction temperature. The reaction

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

takes place and continues until, after 40 to 60 hours, all the carbide is transformed into crude calcium cyanamide. A solid mass results which, after cooling, is crushed, powdered, and sprayed with water to destroy any unchanged carbide, then with oil to diminish its dustiness. The black powder resulting from the operation contains 60 per cent $CaCN_2$ and is used as ingredient in mixed fertilizers without further treatment.

In a round-about way, nitric acid may be produced from cyanamide, by first making ammonia. The cyanamide is placed in autoclaves 21 feet high and 6 feet in diameter and treated with steam [16]; the ammonia generated may later be oxidized by the hot platinum grid contact method, and the nitric oxide absorbed in water. The ammonia itself may be used in various ways, for instance, to make anhydrous ammonia for refrigeration, sulfate or phosphate of ammonia for fertilizers, and nitrate of ammonia for explosives. The reaction in the autoclave is

$$CaCN_2 + 3H_2O \rightarrow 2NH_3 + CaCO_3.$$

The nitrogen fed into the carbide charge is made by liquefying air and boiling off the nitrogen in fractionating columns.[17]

Until the advent of the direct synthetic ammonia process, the cyanamide process held a place of importance in the field of fixation of atmospheric nitrogen; at the present time, it seems more likely that it will retain its importance as a process fixing atmospheric nitrogen in the form of the fertilizer ingredient calcium cyanamide, but not as a producer of ammonia and ammonium salts.

By fusion with salt, carbon, and a little carbide, calcium cyanamide may be transformed to sodium cyanide, which in solution is valuable for the extraction of gold and silver from their ores. (*See also* Chapter 18.)

Calcium cyanamide is also the starting material for a number of organic substances, such as guanidine, urea, dicyandiamide, which have become of great importance.

The installed capacity for calcium cyanamide in Niagara Falls, Ontario, Canada, was (1934) 80,000 tons of nitrogen per year, which is 14.5 per cent of the world total cyanamide capacity; Germany had 36.7 per cent, Japan, 12.9 per cent of it. There is no production in the United States. In 1947, 153,764 short tons of calcium cyanamide were imported from Canada into the United States; in 1946, a still higher total, 163,093 short tons (Bureau of Plant Industry, Soils, and Agricultural Engineering).

The Bucher Process. Soda ash mixed with iron and carbon may be heated in a current of nitrogen, to produce sodium cyanide and a ferrocyanide.[18]

[16] A complete diagram of a plant for generating NH_3 from calcium cyanamide will be found facing p. 394, in "The atmospheric nitrogen industry," Bruno Waeser, trans. by E. Fyleman, Philadelphia, P. Blakiston's Sons & Co., 1926.

[17] Chapter 19.

[18] "The fixation of nitrogen," John E. Bucher, *Trans. Am. Inst. Chem. Eng.*, 9, 335 (1916). For a recent study of this process, see *Ind. Eng. Chem.*, 18, 43 (1926).

The Serpek Process. Certain metals at elevated temperature unite readily with nitrogen while heated to form nitrides, which in a subsequent treatment with steam give up all their nitrogen in the form of ammonia. The best known of these processes is the Serpek, developed on a fair scale in France. It consists of passing a mixture of crude alumina (bauxite) and coal through a rotary furnace one way, while nitrogen (producer gas) passes the other way. The furnace is heated externally by electrical means to a temperature of 1800° C. (3272° F.). The operation is continuous:

$$Al_2O_3+3C+N_2 \rightarrow 2AlN+3CO.$$

On treatment with dilute alkali, ammonia is formed, together with a very pure alumina

$$AlN+3H_2O \rightarrow Al(OH)_3+NH_3.$$

If the demand for the by-product were greater, this process would undoubtedly find more general application.[19]

The 1948 quotation for anhydrous ammonia, in tank cars, fertilizer grade, was $68 to $70 a ton.

Nitric Acid from Ammonia

A considerable portion of the ammonia produced by the direct synthetic process is changed into nitric acid by catalytic oxidation. The platinum-catalyzed ammonia oxidation process was originally developed to eliminate the dependence on Chilean saltpeter as the raw material for nitric acid manufacture, but it is now by far the more important source. The ammonia oxidation process was firmly established on a commercial scale in the early twenties in what is now known as the low-pressure process.[20] The principle of the method is as follows: Air at blower pressure, slightly above atmospheric, is mixed with 10 to 11 per cent by volume of gaseous ammonia and passed through a fine screen of red-hot platinum gauze; the ammonia is converted to nitric oxide according to the reaction:

$$4NH_3+5O_2 \rightarrow 4NO+6H_2O+\text{heat}.$$

The oxidation takes place at an extremely rapid rate with as much as 97 per cent of the ammonia converted. The time of contact is 0.0014 second. A great deal of heat is evolved so that the required temperature of the gauze is easily maintained. The products leave the converter at a high temperature. The nitric oxide is oxidized to the dioxide by the excess air present. The reaction is:

$$2NO+O_2 \rightarrow 2NO_2+\text{heat}.$$

This is a slow reaction which is favored by cooling the gases and by delay chambers, which provide the necessary time for near-completion of the oxidation.

The gases then pass through a series of several absorption towers counter-

[19] "The fixation of nitrogen as aluminum nitride," H. J. Krase, J. G. Thompson, and J. Y. Yee, *Ind. Eng. Chem.*, 18, 1287 (1926), contains all the older references.

[20] *Ind. Eng. Chem.*, 23, 860 (1931).

current to a flow of weak acid, which increases in strength to a maximum of 50 to 55 per cent HNO_3 before being discharged. The absorption reaction is:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO + \text{heat.}$$

The NO formed is oxidized to NO_2 again in the towers, and gradually nearly all of it is absorbed.[20] The air necessary to the oxidation and re-oxidation of the NO is present in the original ammonia-air mixture. The heat liberated in the absorption reaction must be removed to produce acid of maximum strength.

Because of the low pressure in the absorption system, the towers may be constructed of stoneware or acid-resistant brick, and the power required to supply the large amounts of air needed is moderately low. On the other

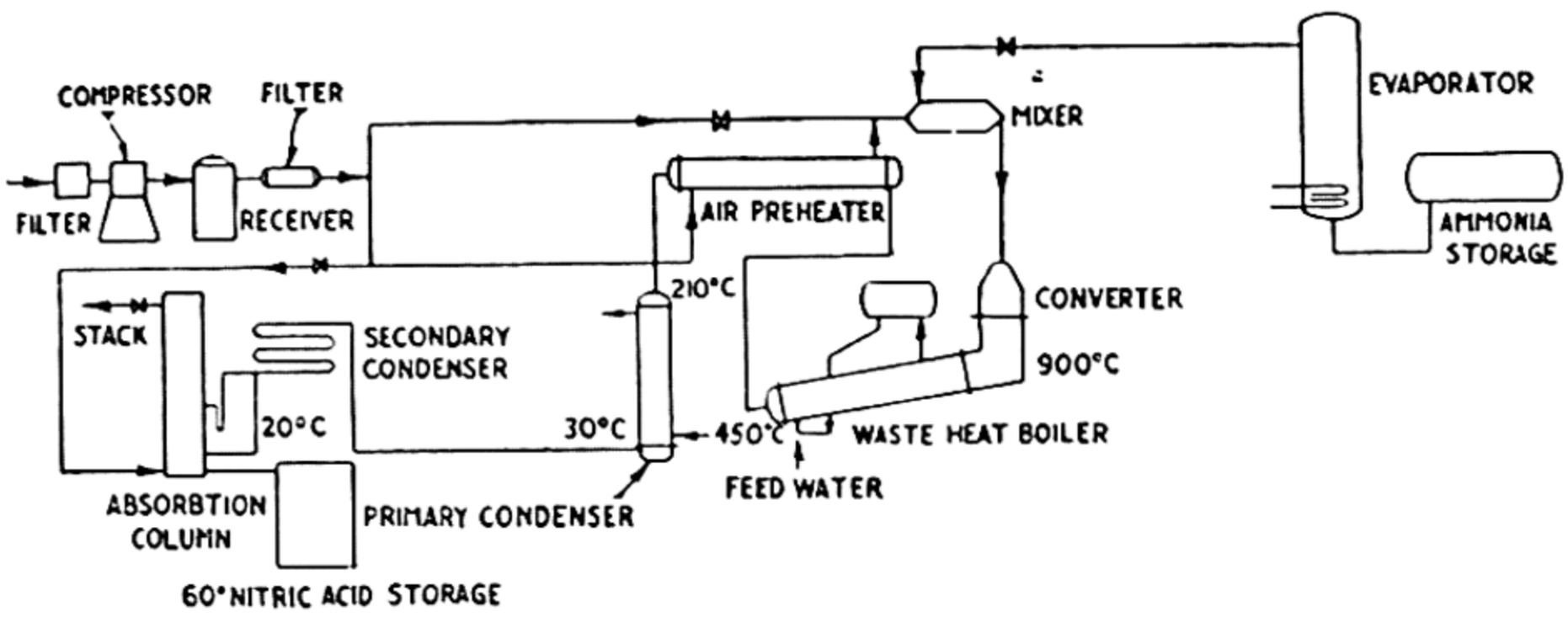


FIGURE 49.—Flow sheet of ammonia oxidation plant. *Ind. Chemist,* 23, 24 (1947).

hand, the development, just prior to 1930, of a high-strength alloy[21] resistant to the corrosive attack of nitric acid at high temperatures offered the possibility of operating the process at pressures up to 100 lbs./sq. in. It was early recognized that higher pressures, while not affecting the ammonia conversion appreciably, would increase the maximum strength of the acid to over 60 per cent, while shortening the time required for the $NO-NO_2$ reaction, and increasing many fold the capacity of a given plant. During the last decade, several designs for such units have been evolved; the most important ones today are the Chemico[22] and the DuPont.[23]

The High-Pressure Unit. A typical high-pressure converter-absorber unit is rated at 55 tons of nitric acid (as 100 per cent HNO_3) per day. The pressure in the reaction zone of the converter is maintained at 100 to 103 lbs./sq. in., while in the absorption tower it is about 70 lbs./sq. in. When operated at rated capacity, 7400 lbs. of acid at 62 per cent strength are

[20] The last traces of NO_2 may be absorbed in sodium carbonate solution in auxiliary towers; a solution of sodium nitrate is thus made.

[21] Called "high-chrome iron"; approximately 17 per cent Chromium, less than 0.15 per cent Carbon.

[22] Chemical Construction Corpn., New York. Pictured in the 1942 edition, page 127.

[23] "Manufacture of nitric acid by the oxidation of ammonia," G. B. Taylor, T. H. Chilton and S. L. Handforth, *Ind. Eng. Chem.*, 23, 860 (1931), with a flow sheet of a semi-works pressure plant.

produced each hour. Air compressors capable of supplying 5400 to 6000 c.f.m. (free air [24]) at 115 lbs./sq. in. pressure are a part of the unit.

Liquid ammonia at an unvarying pressure in the range 175 to 180 lbs./sq. in. is vaporized and filtered to remove contaminants, such as oil or iron oxide, which would be detrimental to the performance of the catalyst. It is then mixed with air which has been preheated to a temperature of 280 to 300° C. The pressure of the air must be carefully controlled by automatic means to prevent even minor fluctuations in the ammonia-air mix ratio, once this has been set by the manually operated control valves. This ratio is determined and controlled by periodic gas analyses at a value in the

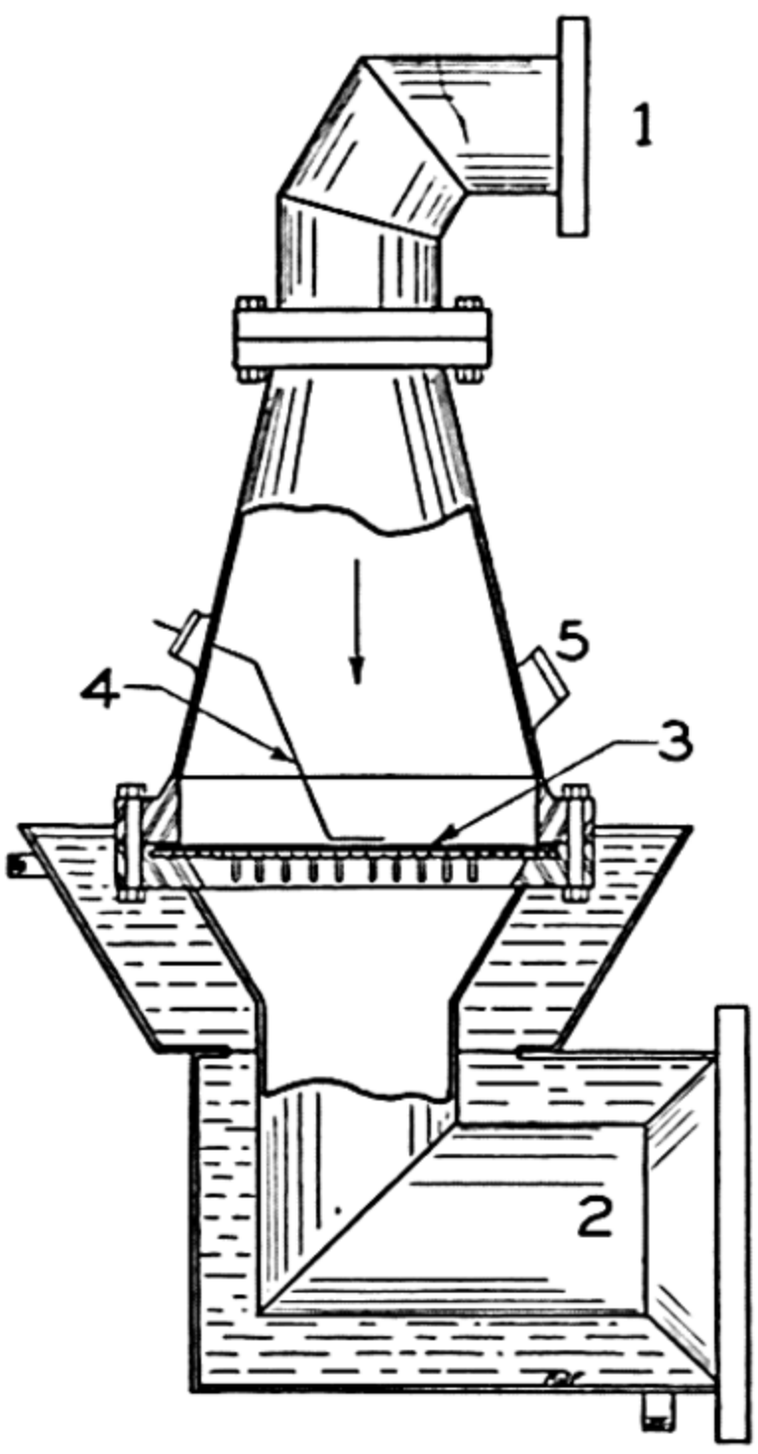


FIGURE 50.—An ammonia converter, showing: 1, inlet for gas mixture; 2, outlet for reacted gases; 3, platinum gauzes; 4, heating element for starting up; 5, sight glass for observing color of catalyst gauze. (From various sources.)

range 9.5 to 10.5 per cent NH_3 by volume. Mixtures with more than 10.8 per cent NH_3 are explosive at 100 lbs./sq. in. pressure. The mixing pipe is constructed of stainless steel or nickel and is suitably baffled.

The mixture is then passed downward through a horizontal pad made up of some 20 layers of 80-mesh gauze. Each gauze sheet is made of 0.003-in. diameter wire drawn from 10 per cent rhodium, 90 per cent platinum alloy,[25] and is in the shape of a hexagon 16 in. across flats. The total weight of gauze used in the pad is critical for attaining maximum conversion; for this unit about 105 ounces would be required. The temperature of the gauze in operation depends upon preheat temperature and mix ratio, and these should be controlled so as to result in a gauze temperature in the range 900 to 930 ° C., to obtain conversions above 94 per cent. At such temperatures, a certain, though small amount of alloy is carried away with the

[24] Air compressors are usually rated by relating their actual output (displacement per minute) to the equivalent volume of air at 14.7 p.s.i., 62° F.

[25] U. S. Patent 1,706,055. With unalloyed platinum, the gauze loss is doubled.

flowing gases as a result of thermal and mechanical stresses in the wire; the higher the temperature, the greater the loss. Provision is made to recover part of the metal dust by means of a glass-wool filter[26]; the gauze weight decreases approximately 0.7 ounce per day at the 55-ton rate.[27] New layers of gauze must be added periodically to maintain peak conversion efficiency. The gauze pad is supported against the aerodynamic drag to which it is subject by a grid of heavy "Nichrome" bars. The converter top is stainless steel, the bottom high-chrome iron; one or both are water-jacketed.[28]

The hot gases leaving the converter are a mixture of NO, H_2O, O_2 and N_2. They are cooled by heat-exchange with incoming air and again with the cool (30° C.) gases leaving the top of the absorption tower. Further cooling is accomplished in water-cooled S-bend tubes; here the nitric oxide and part

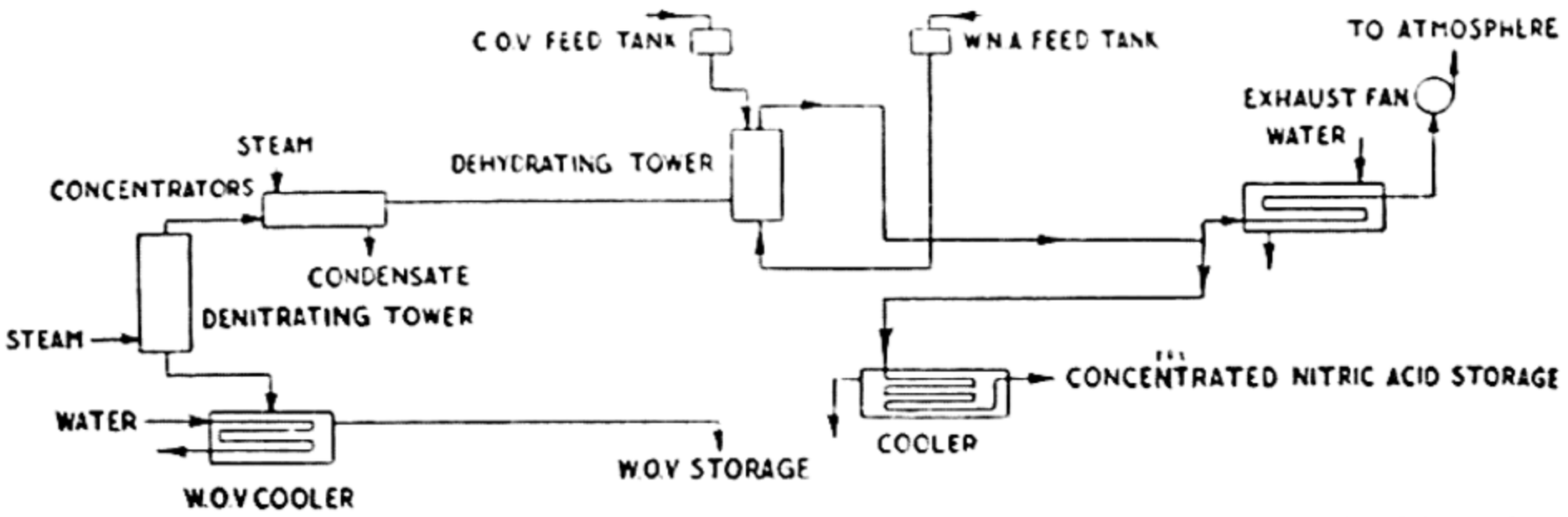


FIGURE 51.—Concentration of nitric acid shown schematically. *Ind. Chemist*, 23, 17 (1947).

of the residual oxygen have time to react to form NO_2; much of the water condenses out, absorbing at the same time enough NO_2 to result in the production of 40 per cent nitric acid. The cooled gases now enter, near the base, a 5¼ foot diameter, 35-plate bubble-cap tower which is fed at the top by chloride-free water.[29] The 40 per cent acid from the cooler-condenser (S-bends) is added to the tower at one of the lower plates. Each plate is provided with cooling-water coils which remove the heat of solution of NO_2 in water. Enough space is allowed between plates to provide time for the NO generated by the absorption reaction to be reoxidized. The strong nitric acid will be colored by its small content of dissolved NO_2. About 14 per cent of the air-compressor output is diverted to the base of the tower to bleach the acid by desorbing the dissolved dioxide, and at the same time to provide additional oxygen for part of the $NO-NO_2$ reaction which takes place in the tower.

The pressure of the spent gases leaving the top of the absorber represents a considerable amount of energy, which can be utilized to produce nearly

[26] U. S. Patents 2,226,113 and 2,226,149.

[27] Without recovery, this would represent a cost of $35 per day, or $0.60 per ton of HNO_3. Gauze loss is less in low-pressure converters.

[28] At temperatures above 400°C., stainless steel catalyzes the reaction $2NH_3+O_2 \rightarrow 2N_2+6H_2O$.

[29] Usually steam condensate, well cooled. Chlorides cause corrosion of the high-chrome iron alloy.

40 per cent of the compressed air requirements. To do this, the tower gases are heated from 30° C. to 200 to 250° C. by interchange with the hot converter gases, and used to operate a two-stage compressor which has a rating of about 2000 c.f.m. The balance of the air is supplied by one or more electrically driven two-stage compressors. The air from both machines must be filtered to remove entrained oil. The power requirement with the power-recovery compressors operating is about 190 kilowatt-hours per ton of 100 per cent HNO_3.

The overall yield obtained under these conditions is in the range 91 to 94 per cent, a 2 to 4 per cent loss occurring due to the presence of unabsorbed NO_2 in the spent gases.[30] Higher yields can be obtained if the unit is operated at a reduced rate. The 62 per cent acid is discharged through a pressure trap to storage tanks which are constructed of 18-8 "stabilized" stainless steel sheet.[31] All the equipment downstream of the converter, including the absorption tower, is fabricated of high-chrome iron alloy.[32]

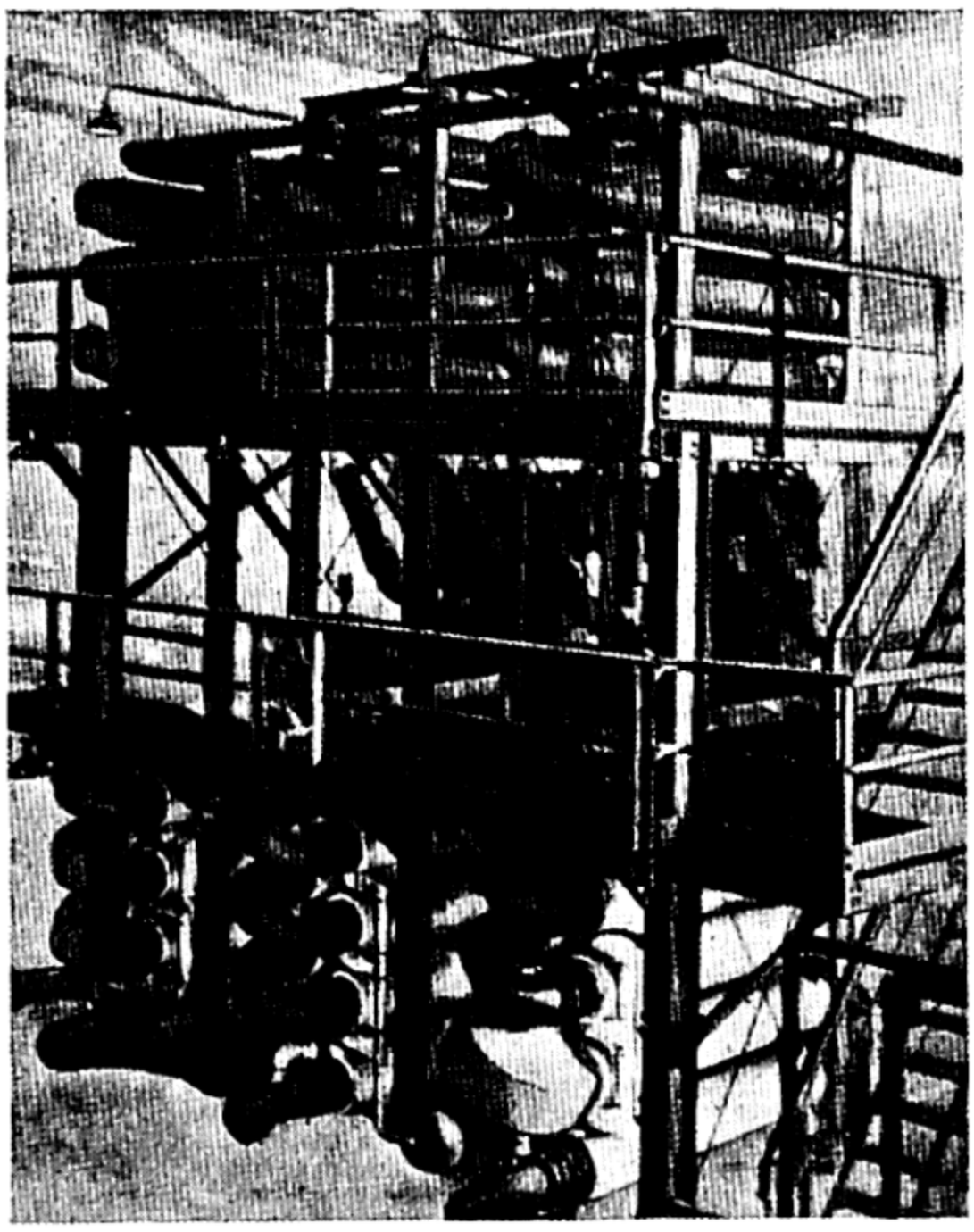


FIGURE 52.—Equipment for the concentration of nitric acid; jacketed pipes for distilling the nitric acid from the sulfuric-nitric acid mixture. *The Ind. Chemist,* 23, 23 (1947).

For many purposes, 50 per cent or 60 per cent nitric acid is satisfactory as to strength; for nitrations of all kinds, it must be stronger. This necesitates an additional operation.

Concentrated Synthetic Nitric Acid. The 50 or 60 per cent HNO_3 is concentrated to 98 or 95 per cent by adding 66° Bé. sulfuric acid, and distilling from a retort; the nitric acid passes out, while the water is retained by the

[30] Reactions producing elemental nitrogen also contribute to lower efficiency: $4NH_3+3O_2 \rightleftarrows 2N_2+6H_2O$, $4NH_3+6NO \rightleftarrows 5N_2+6H_2O$, $2NH_3 \rightleftarrows N_2+3H_2$, $2NO \rightleftarrows N_2+O_2$.

[31] Nitric acid corrodes ordinary stainless steel at welded joints unless the welds are heat treated; for field erection, Type 316 or 321 stainless sheet is used. The "stabilizers" are columbium or titanium added to the alloy.

[32] This alloy must be heat treated after fabrication, so that it may resist corrosion.

sulfuric acid, which becomes 75 per cent acid. This is concentrated in one of the standard sulfuric acid concentrators. Instead of a retort, a Pauling tower may be used, fed with the mixed acid at the top, and steam at the bottom. Another apparatus is the continuous retort system, "Chemico," consisting of a series of steam-jacketed, acid-proof iron pipes. (*Read also* "Salt Cake" in Chapter 3, and "Nitric Acid" in Chapter 2.)

Synthetic sodium nitrate: The nitric acid from ammonia oxidation may be neutralized with soda ash, to give synthetic sodium nitrate. Caustic residues and comparatively weak lots of acid may be utilized in this way.[33]

Sodium nitrite is made by absorbing nitrogen oxide in soda ash solution; the method involves mixing mother liquor with soda ash solution and treating with the gas. The nitrate-nitrite is crystallized out.[34] By regulating the air ratio a composition close to the theoretical N_2O_3 may be secured and comparatively pure nitrite obtained. It is purified by crystallization. An older method for making sodium nitrite is given in Chapter 31.

Fauser Process[35] for Concentrated Nitric Acid from Ammonia in a Single Step. It is highly desirable to find a way to manufacture the strong acid directly from the gases issuing from the converter, avoiding the concentration by means of sulfuric acid. This is accomplished in the Fauser process. The reacted gases leaving the converter are cooled rapidly, in order to condense and trap away the water of reaction. The nitric oxide (NO) first formed remains, for the greater part, unoxidized under these conditions. It passes to an oxidation tower, where NO_2 and N_2O_4 form, then to a cooling tower operated at $-10°$ C. (14° F.) and 10 atmospheres; in addition to the gases, the proper amount of dilute nitric acid is introduced at the top of the tower. There passes out at the bottom a mixture of liquefied N_2O_4 and dilute acid, which is pumped into an autoclave. After the charge is in, the temperature is raised to 70° C. (158° F.), and oxygen, under a pressure of 50 atmospheres, is introduced. In 4 hours, the reaction

$$2N_2O_4+2H_2O+O_2 \rightarrow 4HNO_3+18.8 \text{ Cal.},$$

has gone to completion; the acid is 98 per cent or better.

Other Patents

U. S. Patents 1,845,050 and 1,845,068, methods and apparatus for conducting exothermic gas reactions; the incoming gas mixture while being preheated, is in contact with a preliminary amount of catalytic mass. 1,855,040, in which two separate reaction bombs are used, one for purifying and one for producing. Each of these 3 patents has drawings showing construction of converters suitable for the ammonia synthesis. 2,052,326, catalytic converter and ammonia synthesis; 2,010,235, catalytic oxidation of ammonia; 2,018,760, catalyst for ammonia oxidation and the like; French Patent 848,694, on ammonia synthesis; Russian Patent 52,384, on iron catalyst; U. S. Patent 2,234,169, converters for ammonia synthesis or oil hydrogenation, to Eugene J. Houdry and Raymond C. Lassiat. On oxidation of ammonia, U. S. Patent 2,231,202, and Canadian Patent 394,134.

[33] For sodium nitrate hard pellets, see Chapter 8.

[34] U. S. Patent 2,032,699; the proportion of NO_2 and NO formed from the NO and O_2 and N_2 mixture leaving the platinum converter depends upon the rapidity of cooling.

[35] *Chem. Met. Eng.*, 39, 430 (1932), with a diagrammatic flow-sheet.

Problems

1. A direct synthetic ammonia plant produces 1 ton of NH_3 per hour in a catalyst chamber with a catalyst volume of 10 liters. Assuming perfect conversion, and no losses, what is (a) the weight of hydrogen needed; what is its volume at 0° C. and 1 atmosphere? Using the simple gas laws, what is (b) the volume of the same amount of hydrogen as for (a), for the following conditions: 100° C. and 1 atm.; 100° C. and 100 atm.; 100° C. and 1000 atm.; 300° C. and 1000 atm.? The formula to be used is $pv = NRT$, N is the gram mols, R is the gram molecular gas constant and equals 0.082154; T is absolute temperature; p is given, in atmospheres; with these figures, the answer will be in liters. $3H = 3.024$; $NH_3 = 17.032$.

Answer: (a) 1,791,900 liters; (b) 3761.1 liters at 300° C. and 1000 atm.

2. The volumes computed in 1 give a good representation of the enormous decrease in volume due to the high pressures, in spite of the high temperature. These volumes are not correct, however, because hydrogen does not follow the gas law exactly. In order to find the true volume, compressibility coefficient must be used, which rests on experiments. By means of the compressibility coefficient, the volume in cc. for one gram of the gas is computed; knowing the weight, the total volume may be obtained readily.†

	Hydrogen	Nitrogen	N_2+3H_2	Ammonia
0° C. and 1 atm.	1	1	1	1
100° C.; 1 atm.	1.3660	1.3669		1.379
100° C.; 100 atm.	1.4356	1.4121	1.4362	*
100° C.; 1000 atm.	2.0844	2.4948	2.1870	*
300° C.; 1000 atm.	2.8157	3.3203	2.9504	....

* The critical temperature for NH_3 is 132.4° C., the critical pressure 115 atmospheres; explain why the data are missing.

The compressibility factor is used as follows: For 100° C. and 1000 atm., for hydrogen its value is 2.0844. Then

$$v = \frac{2.0844}{1000} \times \frac{22{,}428}{2.016} = 23.20 \text{ cc. per gram.}$$

Compute the volume for hydrogen for the conditions stated in Problem 1, and list the results opposite the results from 1.

Answer: For hydrogen, for 300° C. and 1000 atm., corrected: 5045.6 liters.

3. Perform the same computations for nitrogen, and for the mixed gases as represented by $N_2 + 3H_2$. The apparent molecular weight for this mixture is 8.516.

4. With a conversion of 40 per cent, the amount of hydrogen computed above in 1 and 2 is only a part of a larger total. What is this total? What is the volume of the exit gases, expressed for standard conditions (the ammonia assumed to remain gaseous)?

5. In a regular run for direct ammonia, the space velocity is 39,600. The hydrogen-nitrogen gas mixture is 3 hydrogen and 1 nitrogen. The catalyst volume (apparent volume) is 10 liters. The conversion is 40 per cent, and there are no losses. In which period of time will 1 ton of NH_3 be made? And in that period, what is the volume of raw gases which must be sent into the converter, in order to give the performance specified? Express this quantity for standard temperature and pressure (0° C. and 1 atm.); find its volume for 300° C. and 1000 atm., which will be the working conditions, in two ways, first according to the simple gas laws, second, using the compressibility coefficients given under Example 2.

Note: The apparent molecular weight of the $3H_2 + 1N_2$ gas mixture is 8.516.

Answer: 12 hours is the period of time.

6. In the Fauser process for direct ammonia, the reaction for preparing the needed nitrogen is $2NH_3 + 2.5O_2 \rightarrow 2NO + 3H_2O$. The oxygen brings with itself the nitrogen which air contains. Is the statement and the figure of 10 given in the text correct, and is it per cent by volume or by weight which is meant?

† H. A. Curtis, "Fixed Nitrogen," p. 241, New York, Chemical Catalog Co. (Reinhold Publishing Corp.), 1932.

Reading References

"Fixed Nitrogen," H. A. Curtis, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1932.

"Plant and operating costs with the low pressure Mont Cenis process," W. F. Scholvien, *Chem. Met. Eng.*, 38, 133 (1931).

"The processes of George Claude for the synthesis of ammonia," Jean Delorme, 2nd Int. Conf. Bit. Coal, 1928, v. 2, p. 223.

"Synthetic ammonia plant at Ostend (Casale)," F. A. F. Pallemaerts, *Ind. Eng. Chem.*, 21, 22 (1929); *Proc. Intern. Conf. Bituminous Coal, 2nd Conf.*, 2, 178 (1928).

"The high pressure chemical engineering equipment of the chemical research laboratory, Teddington (England)," Harold Tongue, *Trans. Inst. Chem. Eng.* (English), 8, 81-97 (1930). Profusely illustrated.

"High pressure reactions," W. A. Bone, *Trans. Inst. Chem. Eng.* (English), 8, 98-106 (1930). Illustrated.

"Pressure-synthesis operations of the Du Pont Ammonia Corporation," *Ind. Eng. Chem.*, 22, 433 (1930).

"Manufacture of nitric acid by the oxidation of ammonia," Guy B. Taylor, T. H. Chilton and S. L. Handforth, *Ind. Eng. Chem.*, 23, 860 (1931).

"Concentrated nitric acid by direct synthesis avoids absorption," G. Fauser, *Chem. Met. Eng.*, 39, 430 (1932).

"Modern nitric acid production demands special alloys," Th. McKnight, *Chem. Met. Eng.*, 39, 490 (1932).

"The gauze catalyst in ammonia oxidation," G. A. Perley and M. W. Varrell, *Ind. Eng. Chem.*, 21, 222 (1929); and "Temperature control in ammonia oxidation," G. H. Perley and R. P. Smith, *ibid.*, 17, 258 (1925).

"Industrial hydrogen," Hugh S. Taylor, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1921.

"Synthetic ammonia by catalysis," A. T. Larson, *J. Chem. Educ.*, 3, 284 (1926).

"Increasing ammonia production with improved catalysts," A. T. Larson, *Ind. Eng. Chem.*, 16, 1002 (1924).

"A direct synthetic ammonia plant," F. A. Ernst, F. C. Reed, and W. L. Edwards, *Ind. Eng. Chem.*, 17, 775 (1925) (the American Process).

"Industrial nitrogen compounds and explosives," G. Martin and W. Barbour, Chapter 4, on the cyanamide industry, London, Crosby Lockwood, 1917.

"The world's inorgànic nitrogen industry," F. A. Ernst and M. S. Sherman, *Ind. Eng. Chem.*, 19, 196 (1927), with valuable statistics.

"Commercial oxidation of ammonia to nitric acid," Charles L. Parsons, *Ind. Eng. Chem.*, 11, 541 (1919), and "Nitric acid from ammonia," by the same author, *Ind. Eng. Chem.*, 19, 789 (1927), both illustrated.

"Pioneering chemical and fertilizer production in Western Canada," S. D. Kirkpatrick, *Chem. Met. Eng.*, 38, 626 (1931).

"Catalysts for oxidation of ammonia to oxides of nitrogen," S. L. Handforth and J. N. Tilley, *Ind. Eng. Chem.*, 26, 1287 (1934).

"Chemical Nitrogen, a survey of processes, organization, and international trade, stressing factors essential to tariff consideration," **Report 114,** second series, *United States Tariff Commission* (1937). This report is really a book of 300 pages. (For sale by the Superintendent of Documents, Washington, D. C., 25 cents.)

"A western nitrogen fixation plant," by G. N. Westby, *Ind. Eng. Chem.*, 22, 1099 (1930).

"Ammonia synthesis at T.V.A.," *Chem. Met. Eng.*, 50, 150 (1943).

"Ammonia, its production from natural gas," by Guy S. Mitchell, *Petroleum Refiner*, 25, 245 (1946).

"Nitric acid production," F. E. Warner, *The Industrial Chemist*, 23, 17 (1947).

In the years 1938 and 1939, the production of phosphate rock in Africa topped the production in the United States, which up to that time had been supreme. In recent years, United States production has increased so greatly that it is again first.

Man eats lime and phosphates in order to have the mineral materials for his teeth and bones. Phosphate pebble deposits are the legacy to man from prehistoric animals, who perhaps did not live in vain, since thanks to their having lived, there is a supply of this essential element (phosphorus) at man's disposal. The same phosphate radicals which perform so useful a function in man's body, did likewise for the humble dwellers of the earth in prehistoric times.

Chapter 7

Phosphates, Phosphoric Acid, Baking Powders

The phosphates for fertilizers, phosphoric acid and its products, and for phosphorus come from two sources: bone ash, and mineral deposits, both more or less pure tricalcium phosphate. Bone ash is purer than the mineral material, as one would expect, and serves for making phosphoric acid and monocalcium phosphate for baking powders, as far as its limited supply allows; and the mineral phosphate is the material for superphosphate, of which 7,372,104 tons were manufactured in the United States in 1945, an all-time high until that year. The mineral often referred to as tricalcium phosphate generally is a complex compound, more or less well preserved and formed, known as fluor apatite, $3Ca_3(PO_4)_2 \cdot CaF_2 \cdot CaCO_3$.

New deposits of mineral phosphate material have been discovered gradually in the course of the past 50 years; they are indicated by the corresponding production figures listed in Table 21.

TABLE 21.—*Main producing countries of natural phosphates in the world in metric tons, for the year indicated.**

French Morocco	1,635,000	(1945)
Tunisia	706,340	(1945)
Algeria	220,349	(1944)
Egypt	318,185	(1944)
Nauru and Ocean Islands	1,263,385	(1940)
French Oceania	200,000	(1944)
U.S.S.R. (apatite)	2,000,000	(1941)
Sweden (apatite)	150,000	(1944)
United States (sold or used by consumers)	5,899,921	(1945)

* "Minerals Yearbook," 1945.

Within the United States, the mineral phosphate deposits are: Florida land pebble (30 to 36 per cent P_2O_5), Tennessee brown rock (25 to 37 per cent P_2O_5), Florida hard rock (25 to 37 per cent P_2O_5), Tennessee blue rock (27 to 33 per cent P_2O_5), Western rock (26 to 32 per cent P_2O_5), soft and waste pond phosphates of Florida (15 to 35 per cent P_2O_5).

As the percentage figures for the phosphoric acid content (P_2O_5) indicate, there is a variation in the quality of the phosphate deposits. High-grade rock contains 70 to 80 per cent tricalcium phosphate; the impurities are

mainly clay, limestone, sand and calcium fluoride.[1] The Florida[2] land pebble is high grade, and is found on the bottom and along the banks of rivers and lakes. The pebbles on river bottoms are gathered by scoops, and are washed and dried in rotary cylinders; the banks are mined hydraulically and at the same time the pebbles are washed free from clay and earth, and then dried. Tennessee[3] brown rock is also high-grade, but has a greater impurity of iron and alumina[4]; both the brown rock and blue rock are actively exploited. The washing is done in a variety of ways, among others by stirring the crushed rock with water and running off the lighter clay suspension. The western rock is somewhat lower in grade, and contains much organic matter (7 per cent); by roasting the rock before using it for superphosphate, the phosphoric acid content is raised, and a waste of sulfuric acid is avoided. All phosphate rock deposits occur in beds a few feet thick; thus for Tennessee, the average is 6 to 8 feet. The Tunisian mine near Gafsa and the Algerian[5] deposit near Tebessa have beds varying from 2 to 10 feet in thickness. Less extensive deposits occur in Spain, and in the Somme region, in France.

TABLE 22.—*Salient statistics of the phosphate-rock industry in the United States for 1945.**

	Long tons of rock	P_2O_5 content	Average value at mines
Production (mined)	5,399,739	1,737,185	
Sold or used by producers			
Florida			
Land pebble	4,103,022	1,382,950	$3.80
Soft rock	71,715	15,050	4.09
Hard rock	63,491	22,613	6.71
Tennessee	1,294,297	375,370	4.68
Idaho	123,340	38,984	5.46
Montana	150,858	49,068	6.07
Virginia (included with Tennessee)			
Total United States	5,806,723	1,884,035	4.12

* "Minerals Yearbook," 1945.

Finely ground phosphate rock has been used for direct application to the soil, but the amount is slight compared to superphosphate tonnage.[6]

A defluorinated phosphate is being produced for use in animal feeds to replace bone meal.[7]

[1] Ratio of fluorine to phosphoric acid is constant, for a given deposit; see *Chem. Met. Eng.*, 21, 1253 (1929).

[2] One district lies along the Charlotte Harbor and Northern Railway which runs through Charlotte, De Soto, Hordee, and Polk counties; another is near Dunellon, in Marion County.

[3] Maury, Hickman, and Lewis counties.

[4] These impurities may be reduced by applying flotation methods; K. D. Jacob, *Ind. Eng. Chem.*, 23, 15 (1931); in superphosphate, iron and aluminum oxides favor reversion.

[5] *Chem. Abstracts*, 19, 1551 (1925).

[6] U. S. Department of Agriculture Yearbook, 1939, p. 513. See also "Availability of phosphate rocks in soils of varying degrees of acidity," by R. P. Bartholomew, *J. Am. Soc. Agronomy*, 29, 293 (1937).

[7] "Minerals Yearbook," 1940; see also Technical publication 695, "Phosphate fertilizers by calcination process—volatilization of fluorine from phosphate rock at high temperatures," by K. D. Jacobs, D. S. Reynolds, and H. L. Marshall, *Am. Inst. Min. Met. Engineers* (1936); and "Report on phosphoric acid, availability of calcined phosphate and other new phosphatic materials as determined by chemical and vegetative tests," by Wm. H. Ross and K. D. Jacob, *J. Ass'n. Official Chemists*, 232-249 (1937).

The production by states is shown in Table 22.

Superphosphate. Superphosphate is made by the action of chamber acid (50° to 55° Bé., corresponding to 62 to 70 per cent H_2SO_4) on tricalcium phosphate, the essential constituent of phosphate rock. The amount of acid is so regulated that the monocalcium phosphate is formed; it is soluble in water:

$$Ca_3(PO_4)_2+2H_2SO_4+4H_2O \rightarrow \underset{\textit{mono-calcium phosphate}}{CaH_4(PO_4)_2}+2\underset{\textit{gypsum}}{(CaSO_4\cdot 2H_2O)} \qquad (1)$$

Calcium sulfate in the form of gypsum remains mixed with the monocalcium salt, and it is this mixture which constitutes superphosphate. A certain amount of dicalcium phosphate, $CaHPO_4$, insoluble in water, is formed also, and is determined in the analysis by virtue of its solubility in ammonium citrate, in which any unchanged tricalcium phosphate, $Ca_3(PO_4)_2$, is insoluble, the monocalcium phosphate having been removed by water. The mono- and dicalcium phosphates together constitute the "available phosphate" in superphosphate and amount to 16 to 18 per cent P_2O_5.

What is not generally known is that ordinary superphosphate, and indeed other forms of water-soluble inorganic phosphates, are rapidly converted in the soil into forms which are practically insoluble or are only slightly soluble in pure water. The reaction or reversion results in the formation of water-insoluble calcium, iron and aluminum phosphates, and other insoluble phosphates. These compounds are, nevertheless, able to supply sufficient phosphorus for the growth of plants, partly because of their fine state of subdivision. In general, it may be said that inorganic phosphate fertilizers show very little penetration into the soil beyond the zone in which they are applied, except insofar as this zone is disturbed by plowing and other mechanical means.

To make the superphosphate, the rock is reduced to a powder by means of a jaw-crusher [8] followed by a continuous pebble mill,[8] for example. Equal weights of cold acid (first) and powder are run into a cast-iron mixer equipped with paddles, and able to handle 2 tons of rock in each charge. The mass is stirred for 2 minutes, and quickly dumped into the "den" below, where it remains 24 hours; the reaction started in the mixer continues in the den, and causes a rise in temperature to 100° C. (212° F.). (*See* Fig. 53.) Carbon dioxide and hydrogen fluoride are evolved, thus making the rock porous. The carbon dioxide comes from a limestone impurity:

$$CaCO_3+H_2SO_4 \rightarrow CaSO_4+H_2O+CO_2.$$

The hydrogen fluoride originates in the calcium fluoride present in the rock:

$$CaF_2+H_2SO_4 \rightarrow CaSO_4+2HF.^{9}$$

The gases pass out of the mixer and chamber pits under gentle suction, and reach a spray of water in one or more towers. The hydrogen fluoride

[8] Chapter 44.

[9] Some of the hydrogen fluoride attacks the silica impurity, forming the gas silicon tetrafluoride SiF_4 which passes to the towers where it is decomposed by water; $4HF+SiO_2 \rightarrow SiF_4+2H_2O$ and later with the cold water, $3SiF_4+2H_2O \rightarrow SiO_2+2H_2SiF_6$. Not all the fluorine is violatilized; approximately 75 per cent remains in the superphosphate product (Bur. Agr. Chemistry, 1939).

solution may be neutralized with soda ash, forming sodium fluoride, or it may be treated with more silica (washed sand) to form fluosilicic acid, H_2SiF_6; this may in turn be made into sodium or magnesium silicofluoride, the former an insecticide, the latter a preservative for Portland cement surfaces:

$$6HF+SiO_2 \rightarrow H_2SiF_6+2H_2O; \qquad 2HF+Na_2CO_3 \rightarrow 2NaF+H_2O+CO_2;$$
$$H_2SiF_6+MgO \rightarrow MgSiF_6+H_2O.$$

After the 24-hour period in the den, the mass is removed by conveyors and bucket elevators to the storage piles, where the superphosphate is allowed

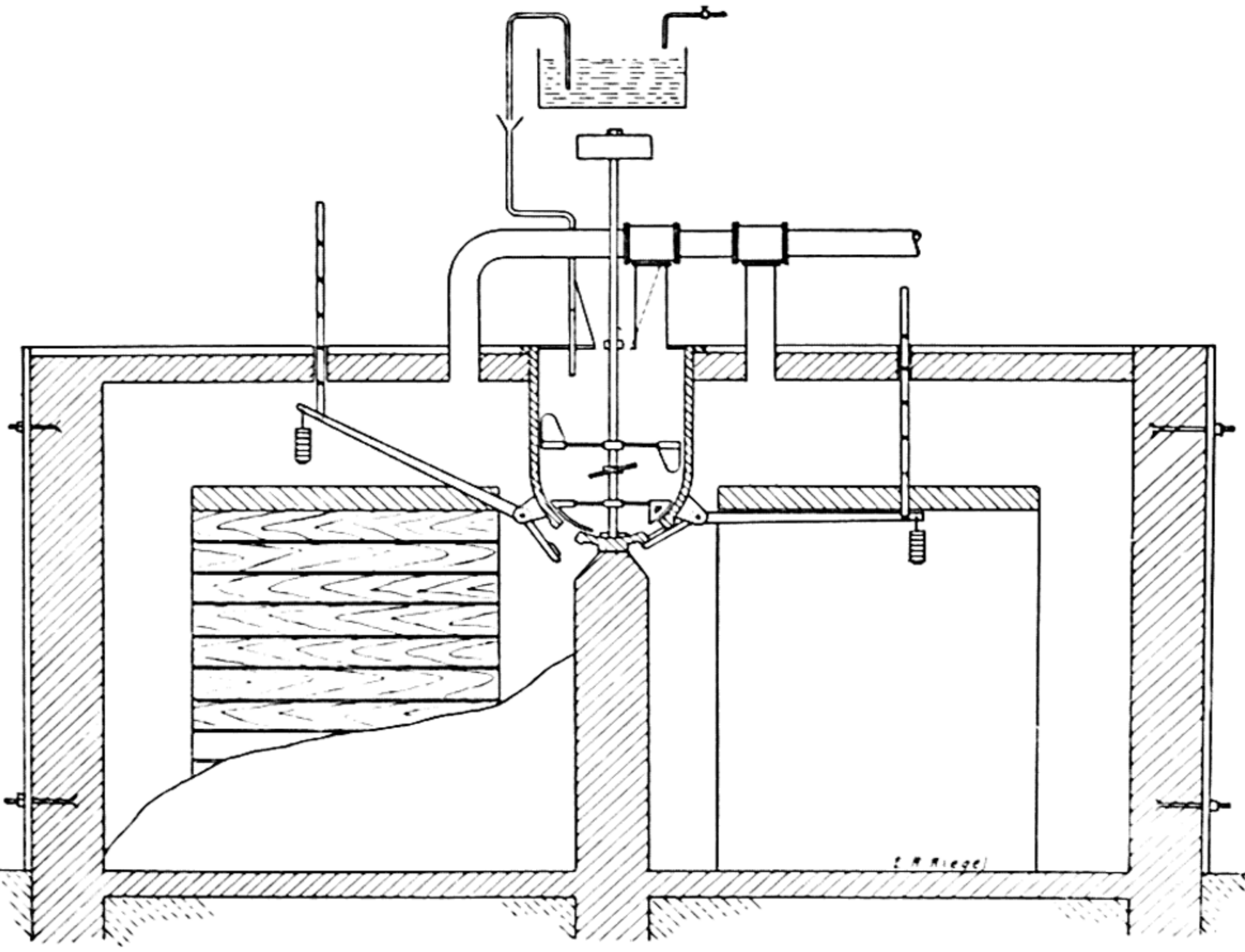


FIGURE 53.—A simple installation for making superphosphate; the mixer serves two pits; outlets for the gases evolved are shown.

to "cure" for 8 to 10 weeks. By "curing" is meant the further reaction of free acid on unchanged portions of the rock. The longer the period of "cure," the less the amount of acid one needs to apply. In other plants, there is no curing; the mass from the den passes the "rasper," which divides it into uniform, fine grains, and from there to the storage pile, ready for shipment.

The amount of sulfuric acid added is a little less than required for the main reaction (1), in order to avoid residual unchanged phosphoric acid. The water is ample to allow complete wetting of the powdered rock; a part of the excess remains as water of crystallization, $CaH_4(PO_4)_2 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$; some passes out during the period spent in the den. The superphosphate weighs considerably more than the phosphate rock taken (for example, it may be as much as 1.70 times the weight of the 75 per cent tricalcium phosphate rock taken), because the sulfuric acid added remains

in the product in the form of gypsum, while most of the water added also remains. There is a loss in fluorine compounds, which pass out, but the extra amount of acid which must be added weighs more than the compounds driven out, so that here again there is a gain in weight. By adjusting the amount of acid, its water content, and perhaps its temperature, to suit the rock used, a product is obtained which is dry, which powders easily, and which does not stick in the drill which applies it to the soil.

It has been proposed to produce a dense, granular superphosphate, whose granules would be mechanically strong, and at the same time shorten the manufacturing process from many days to half an hour. This would be done in a horizontal, rotary autoclave.[10]

Triple Superphosphate. A material with three times as much available phosphate is the triple superphosphate,[11] containing 48 to 49 per cent P_2O_5. It is therefore a far more concentrated product, and as a result transportation costs are lower. It is made by the action on phosphate rock of phosphoric acid instead of sulfuric:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3CaH_4(PO_4)_2.$$

No gypsum is formed, but instead, more of the soluble calcium phosphate. The acid applied contains 45 per cent P_2O_5, because such strong acid introduces less water, which would have to be evaporated later. The reaction of the rock with phosphoric acid is slower than with sulfuric.

The rock and phosphoric acid are mixed for 1 hour; the resulting solid mass is disintegrated and conveyed to the wet-storage building; its moisture content is 20 per cent. After an aging period of 30 days, it is dried at a temperature below 200° C. (392° F.), and ground in a ring-roll grinder to pass a screen with 6 meshes to the inch. It is a stable, non-hygroscopic powder, with 41 to 42 per cent P_2O_5 in the form of water-soluble phosphate, 48 to 49 per cent P_2O_5 as total available phosphate, combined CaO 20.80 per cent, and moisture 2.75 per cent.

Extending the figures for two months in 1946 to a full year leads to an estimated production for that year of 360,000 short tons of "concentrated superphosphate 45 per cent APA" (available phosphoric acid).[12]

Treating ordinary superphosphate with anhydrous ammonia gas permits the fixation of some 3 per cent NH_3 without increasing the consumption of sulfuric or other acid, and gives a product easier to store and apply, which, furthermore, does not rot the containing bags.[13] This has now been extended to treating with urea-ammonia liquor, sodium nitrate-ammonia liquor, and ammonium nitrate-ammonia liquor, with nitrogen content equivalent to 37.5 to 45 per cent nitrogen (compare next chapter).

The available phosphoric acid in fertilizers for United States agriculture in 1946 was 1,566,000 short tons (P_2O_5) (production) compared to the 1940-44 yearly average of 1,104,000 tons.[14]

[10] U. S. Patent reissue 19,825, of original patent 1,947,138.
[11] E. L. Larison, *Ind. Eng. Chem.*, 21, 1172 (1929).
[12] "Facts for Industry."
[13] K. D. Jacob, *Ind. Eng. Chem.*, 23, 14 (1931).
[14] Bureau of Plant Industry, Soils and Agricultural Engineering, Department of Agriculture.

The interesting work carried on at the University of Nevada Agricultural Experiment Station on organo-phosphates has not led to commercial developments.[15]

Phosphoric Acid

Wet Method. The major part of the phosphoric acid produced for all purposes is still made by the action of dilute sulfuric acid, 30° Bé., on ground phosphate rock or bone ash:

$$Ca_3(PO_4)_2+3H_2SO_4+6H_2O \rightarrow 2H_3PO_4+3(CaSO_4\cdot 2H_2O).$$

The calcium sulfate is obtained as gypsum. The reaction may be performed in a lead-lined tank with lead-covered agitator; the calcium sulfate is precipitated, and the clear acid solution containing about 20 per cent P_2O_5 as phosphoric acid is decanted. The mud is washed with water, and the dilute acids obtained concentrated by heat, or used for the dilution of the incoming sulfuric acid from the 50° or 55° Bé. to 30° Bé., ready for treating a new batch. The gypsum may also be filtered in a press, or on sand filters. Improved apparatus has been installed which hastens the separation of the acid from the mud. The Dorr system provides for continuous operation and delivers a first strength of 29 per cent P_2O_5 as phosphoric acid (equivalent to 40 per cent H_3PO_4); a second strength of 15.5 per cent P_2O_5 as acid is employed for the dilution of the chamber or other sulfuric acid. A series of three agitators and six thickeners is used, lined with acid-proof bricks and operated on the counter-current principle; for use in making high-grade fertilizer material, no filtration is required. The mud discharged is free from acid. This artificial gypsum has been utilized for making a number of gypsum products.

When the acid is to be used for baking chemicals, it must be purified from any remaining gypsum, silica, lead, arsenic, iron and aluminum oxides, and fluorine compounds.[16] The crude acid is colored green; the purified acid is colorless.

Concentration is performed in lead vessels, by means of lead steam coils, to a 45 per cent P_2O_5 strength, or 50 per cent, at atmospheric pressure. Care is taken to avoid overheating, to prevent the formation of pyrophosphoric acid, $H_4P_2O_7$. Higher strengths than 50 per cent are more readily obtained by the volatilization process.

The yield by the wet method is about 90 per cent overall.

Thermal Methods. Phosphorus and phosphoric acid may be produced without the aid of sulfuric acid, namely, by thermal methods. On heating tricalcium phosphate in the presence of carbon and silica, elemental phosphorus is liberated which, on oxidation and solution in water, gives phos-

[15] "Phosphate Studies: I. Soil penetration of some organic and inorganic phosphates," V. E. Spencer and Robert Stewart, *Soil Science*, 38, No. 1, 65 (1934); *Proc. Second Dearborn Conference*, (May 1936), p. 37, publ. Chem. Foundation, 654 Madison Avenue, New York. "Organic phosphates: I. Fixation studies with three different soil types," by G. E. Hilbert, L. A. Pinck, M. S. Sherman, and T. H. Tremearne, *Soil Service*, 46, 409 (1938).

[16] U. S. Patent 1,858,203 proposes the boiling of the acid with hydrated silica such as diatomaceous earth, followed by the addition of soda ash and decantation from the sodium fluosilicate produced.

phoric acid. As heating devices, either the electric furnace or the fuel-fired blast furnace may be used. In either case, the reaction which takes place is:

$$Ca_3(PO_4)_2+5C+6SiO_2 \rightarrow P_2+5CO+3(CaO\cdot 2SiO_2).$$

The first product is phosphorus; if it is collected under water, and the oxidation performed later as a distinct step, it is the two-pass system; but if air is allowed to join the phosphorus vapor so that it is at once oxidized to P_2O_5, in the presence of moisture, it is the one-pass system. It should be noted that in the latter, carbon monoxide must also be oxidized, so that the second part of the chemical action is:

$$P_2+5CO+5O_2 \rightarrow P_2O_5+5CO_2.$$

The solution in water:

$$P_2O_5+3H_2O \rightarrow 2H_3PO_4$$

yields the final phosphoric acid.

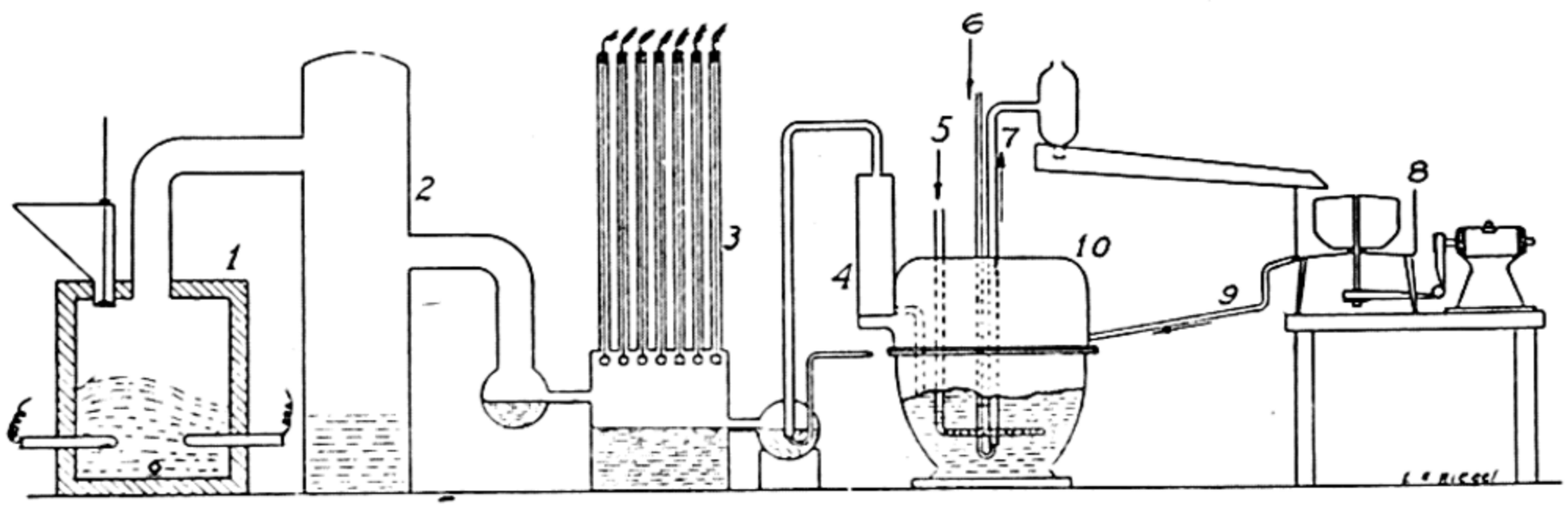


FIGURE 54.—The volatilization process for phosphoric acid, and saturator for ammonium phosphate manufacture; 1, furnace; 2, dust catcher; 3, electrical precipitator; 4, entry of phosphoric acid liquid into saturator; 5, ammonia gas inlet with distributor; 6, compressed air line for continuous ejection of suspension of crystals through 7 to centrifugal 8, with run-back 9 for the clear liquor.

A flow sheet of the volatilization method, with electricity as the source of heat, illustrates the one-pass process. (*See* Fig. 54.) The rock or pebble, crushed to small size, is mixed with sand and coke, and fed to an electric furnace having 3 electrodes. The furnace consists of a cylindrical steel shell lined with fire-bricks; the cover has an outlet for the gases which pass through a wet dust catcher to a Cottrell precipitator wherein the phosphoric acid mist is precipitated. The calcium silicate slag passes out of the furnace at the tap hole; given the proper impurities or additions, the slag may be a valuable cement. The flow sheet includes a scheme for making ammonium phosphate.

A fertilizer plant was included in the development[17] of the Tennessee Valley Authority; in this superphosphates are produced. An electric furnace, using about 4,800 kwh. per ton of P_2O_5 charged, sends its gases (phosphorus and carbon monoxide) (a) to be oxidized together, wasting the carbon monoxide, and giving phosphorus pentoxide, which is then hydrated

[17] "The manufacture of phosphoric acid by the electric furnace method," Harry A. Curtis, *Trans. Am. Inst. Chem. Eng.*, 31, 278 (1935) with illustrations, flow sheet (p. 282), and diagrams.

to the acid; or (b) to a cooler where the phosphorus is condensed as a liquid under water, allowing the carbon monoxide to be burned usefully by itself. The phosphorus is oxidized and hydrated later. The absorption of the P_2O_5 in 85 per cent phosphoric acid runs smoothly and is full of promise.

The temperature at which reduction takes place is 1300° to 1400°C. (2372° to 2552° F.); 40 per cent of the total heat supplied raises the charge to 1300° C. (2372° F.); the 60 per cent which causes the reduction must be supplied above 1300° C. This the electric furnace does well. On the other hand, the extremely high heat of the arc may volatilize lime, silica, alumina, magnesia; a number of ingenious dispositions and inventions have been necessary in order to prevent this difficulty.

In the blast furnace, 2.36 pounds of coke are consumed for each pound of phosphorus pentoxide, P_2O_5, produced. The yield for the thermal methods is 80 per cent; phosphorus is lost to iron and other impurities left in the furnace.

Phosphorus pentoxide is a white powder, extremely hygroscopic. Phosphorus is a yellow, wax-like solid, which melts at 44° C. (111.2° F.); it is kept under water, for in the air it oxidizes spontaneously to its white powdery oxide.

The thermal methods have the advantage of permitting the manufacture of any strength phosphoric acid desired; the higher strengths are obtained without the necessity of concentrating by heat. The acid produced is, furthermore, much purer.

In order to manufacture yellow phosphorus, the electric furnace described under (a) is used. The production in the war year of 1944 was 177,787,000 pounds, allocated as follows: to direct military use, 64,190,000 pounds; to foreign use 5,507,000 pounds; to other uses (domestic), 108,090,000 pounds. Yellow phosphorus, in drums, carload lots, is quoted at 26 cents a pound (May, 1948).

The production of phosphoric acid in 1946 is shown by the following figures:

	Short tons*
Phosphoric acid, total (50% H_3PO_4)	894,615
From phosphorus (50% H_3PO_4)	440,056
From phosphate rock (50% H_3PO_4)	454,559

* "Facts for Industry," Bureau of the Census.

Trisodium Phosphate. Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, is an alkaline substance which has come to be highly prized as a detergent, a water-softener, and boiler compound. It is made in two steps. First, phosphoric acid is neutralized with soda, with the formation of disodium phosphate:

$$H_3PO_4 + Na_2CO_3 \rightarrow Na_2HPO_4 + CO_2 + H_2O.$$

The third hydrogen atom in phosphoric acid is unaffected by soda ash. To the solution of the disodium phosphate, caustic soda is added, with the formation of the trisodium salt:

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O.$$

In a 4000-gallon tank with agitator, 7000 pounds of soda ash are suspended in 900 gallons of hot water or hot wash liquor; phosphoric acid of 45 per cent P_2O_5 content in the proper amount is added at the surface, so that the carbon dioxide evolved may escape more readily.[18] The solution is boiled to remove all carbonate, diluted with mother liquor from previous crystallizations, and filter-pressed hot. In the next step, 1500 gallons of disodium phosphate solution (14.5 per cent P_2O_5 and 13 per cent Na_2O) are treated with some 2800 pounds of sodium hydroxide dissolved in 300 gallons of hot water, and then 1000 gallons more of the disodium liquor of the same strength. The resulting solution is diluted with mother liquor from the crystallizer to a specific gravity of 1.34 to 1.40 at 90° C. (194° F.). It is filter-pressed, and delivered through steam-jacketed pipes to water-cooled crystallizers; the liquor fed in has a temperature of 70° C. (158° F.) and contains 9.25 per cent P_2O_5 and 13.2 per cent Na_2O. The temperature is reduced gradually to 30° C. (86° F.). The crystals formed are centrifuged, dried in a jacketed rotary drier, cooled, and screened.

A spray-congealed grade is made by adjusting the concentration to match that of $NA_3PO_4 \cdot 12H_2O$, and atomizing at the top of a tower; during the free drop of 70 feet, the particles assume a spherical shape and congeal. The product is screened. To reduce caking, a small amount of another salt (NaF, NaCl) may be added.

The preparation of disodium phosphate has been given incidental to the manufacture of trisodium phosphate, at least as far as its solution. In order to obtain the salt, this solution is crystallized, the crystals centrifuged and packed. Disodium phosphate is $Na_2HPO_4 \cdot 12H_2O$ and effloresces (loses water of crystallization) in the air. It is a valuable agent for water softening. The monosodium salt is also made, but in smaller quantities; this is an acid substance, and serves among other things as a baking chemical. By heating the monosodium phosphate NaH_2PO_4, sodium acid pyrophosphate, with better keeping qualities, is obtained:

$$2NaH_2PO_4 + \text{heat} \rightarrow Na_2H_2P_2O_7 + H_2O.$$

The production of the sodium phosphates in 1946 is given in Table 23.

TABLE 23.—*Production of sodium phosphates (1946).**

	Short tons
Monobasic (100% NaH_2PO_4)	11,961
Dibasic (100% Na_2HPO_4)	59,328
Tribasic (100% Na_3PO_4)	94,963
Meta (100% $NaPO_3$)	26,088
Tetra (100% $Na_4P_2O_7$)	52,149

* "Facts for Industry," May 14, 1947.

In 1944, 161,172,000 pounds of trisodium phosphate had been produced Lithium phosphate by-product is discussed in the next chapter.

[18] "Trisodium phosphate, its manufacture and use," Foster D. Snell, *Ind. Eng. Chem.*, 23, 470 (1931).

Monocalcium Phosphate. Monocalcium phosphate is manufactured in considerable quantities, chiefly as a baking chemical. It is made from the purified phosphoric acid, by the addition of selected hydrated lime or limestone:

$$2H_3PO_4 + CaCO_3 \rightarrow CaH_4(PO_4)_2 \cdot H_2O + CO_2.$$

After mixing, the materials are set aside to allow the reaction to become complete; the resulting product is a solid, which is crushed to a medium size. It is then dried at a gentle heat, which causes the loss of the water of crystallization. The dry product is milled to the desired granulation, and packaged; it is practically pure monocalcium phosphate.

Dicalcium phosphate is obtained as a by-product in the manufacture of ossein; *see* Chapter 36.

Ammonium phosphate has the advantage of supplying two of the necessary elements for plant food in a single substance. Monoammonium phosphate is made by passing ammonia into strong, hot phosphoric acid until the composition corresponding to $NH_4H_2PO_4$ has been reached; on cooling, a rich crop of crystals forms; these are centrifuged and dried to a stable, white powder, having the formula $NH_4H_2PO_4$. The flow sheet for phosphoric acid by volatilization illustrates the preparation of this salt.

The *diammonium phosphate*, containing some of the mono salt, is more difficult to prepare. Both are made in increasing quantities, with synthetic ammonia. In the average crop year 50,000 tons of ammonium phosphate (Ammophos) are produced and used in making fertilizers in the United States.

Baking Powders

Baked food products owe their light structure to the presence of carbon dioxide evolved within the dough during its preparation and the early stages of baking. The carbon dioxide may be produced by yeast (bread) or by baking powders (cakes); the latter generate the gas more rapidly, partly at once on being mixed and moistened, the rest on application of heat. A baking powder, then, is a combination of chemicals, called the baking chemicals, which yield the carbon dioxide gas on being moistened. The amount of gas is calculated to be 14 per cent (by weight) for household powders and 17 per cent for commercial powders. The standardization is performed by having the materials stronger than necessary, and diluting them to the right strength by the addition of cornstarch. After gas evolution, the residual chemicals must be without harmful action on the human system. Figure 55 shows the equipment for mixing and weighing the ingredients.

Three types of baking powders are estimated to constitute 90 per cent of all the baking powders produced (U. S.); their quantitative formulas to yield 14 per cent CO_2 are as follows:

	Cream of tartar	Calcium acid phosphate	S.A.S. phosphate
	Per cent		
Sodium bicarbonate	26.73	26.73	26.73
Cornstarch	22.40 (1)	39.84 (2)	40.07 (3)
Tartaric acid	5.97	....	....
Cream of tartar	44.90	....	....
Monocalcium phosphate	....	33.43	13.28
Sodium aluminum sulfate (calcined)	....	....	19.92

In addition to these three, a fourth type (4) is sold to commercial bakers often in the form of the separate unmixed ingredients; when made up, it contains 30.59 per cent sodium bicarbonate, 29.03 per cent cornstarch, and 40.38 per cent sodium acid pyrophosphate, $Na_2H_2P_2O_7$. This powder evolves 17 per cent gas.

It will be noted that all baking powders have the same carbon-dioxide-generating chemical, $NaHCO_3$, and differ only in the acidic substance. The reactions are probably as follows:

$$KHC_4H_4O_6 + NaHCO_3 \rightarrow KNaC_4H_4O_6 + CO_2 + H_2O, \text{ for powder (1)}$$

$$3CaH_4(PO_4)_2 + 8NaHCO_3 \rightarrow Ca_3(PO_4)_2 + 4Na_2HPO_4 + 8CO_2 + 8H_2O, \text{ for powder (2)}$$

$$Na_2Al_2(SO_4)_4 + 6NaHCO_3 \rightarrow 6CO_2 + 4Na_2SO_4 + 2Al(OH)_3, \text{ for part of powder (3)}$$

$$Na_2H_2P_2O_7 + 2NaHCO_3 \rightarrow Na_4P_2O_7 + 2CO_2 + 2H_2O, \text{ for powder (4)}$$

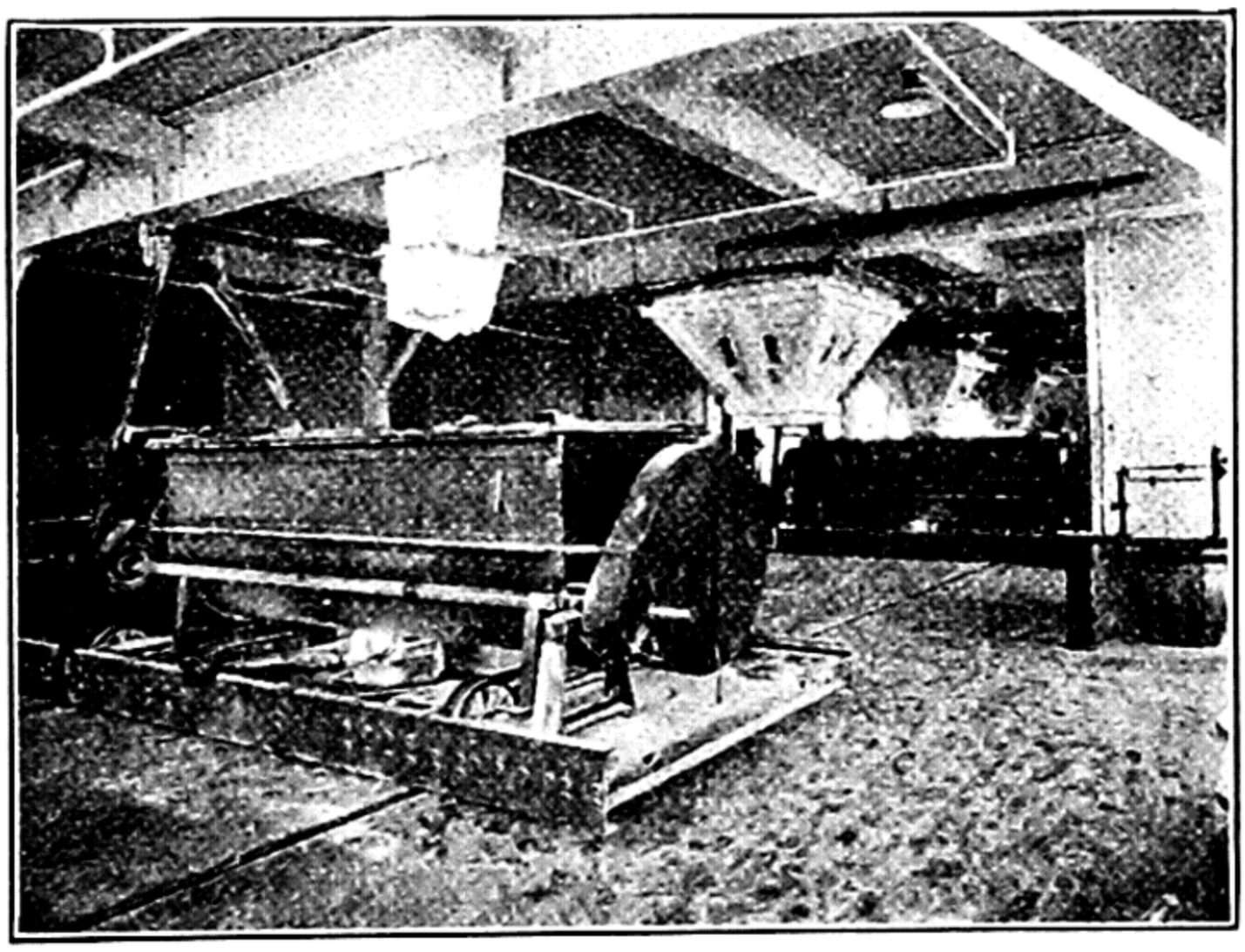


FIGURE 55.—Mixers and weighing hoppers for ingredients for baking powders. The mixers contain 5000 lbs. of baking powder. Note that the mixer is on wheels and may be moved to any one of the bins. (Courtesy of the Rumford Chemical Works, Providence, R. I.)

The manufacture of the baking chemicals has been described in the preceding chapters, except for cream of tartar, $KHC_4H_4O_6$, and tartaric acid, $H_2C_4H_4O_6$. Both are solids, and by-products of the fermentation of wine, during which a deposit forms, called argol. It is collected, dissolved, filter-pressed, decolorized by passing through bone char, and the clear liquor crystallized in shallow vats. The product, after drying and powdering, is pure cream of tartar, $KHC_4H_4O_6$.

Wine lees contain, besides the potassium salt, much of the calcium salt; by treating with sulfuric acid, the calcium is precipitated as sulfate, and the mother liquor may be crystallized to give tartaric acid $H_2C_4H_4O_6$, or, written out to show its structure, $HOOC \cdot (OH)HC \cdot CH(OH) \cdot COOH$. This tartaric acid and the tartrates described are exclusively the dextro-rotatory isomers.[19]

Cornstarch is presented in Chapter 23.

[19] The unraveling of the various forms of tartaric acid was the first achievement of Louis Pasteur, in 1852.

The production of baking powders of all kinds in an average year is in excess of 150,000,000 pounds; that of yeast and other leavening compounds in excess of 225,000,000 pounds.

Other Patents

U. S. Patents: 1,688,112, on trisodium phosphate and its manufacture; 1,633,213, on the use of trisodium phosphate in cleaning, whitening, filling and weighting fabrics; 1,758,448-9, on ammonium phosphate by leaching raw phosphate with an acid; 1,878,997, manufacture of phosphates and phosphoric acid using H_2SO_4; 1,845,876, alumina and alkali phosphates by decomposition with caustic alkali; 1,822,040, diammonium phosphate; 1,831,653, leaching phosphate rock with HNO_3; 1,837,284, producing soluble phosphate using SO_2 and nitrogen oxides; 1,753,478, dicalcium phosphate using by-product HCl on phosphate rock; 2,055,332, purification of sodium metaphosphate; 2,062,866, making sodium phosphate; 2,069,182, the application of sulfonated oil to the mineral concentration for Florida phosphate débris; 1,991,916, method and apparatus for oxidizing phosphorus; 1,988,387, production of phosphorus; 1,869,941, 1,837,329; 1,947,138, reissue 19,825, a rapid method for manufacturing superphosphate.

Problems

1. Seven tons of phosphate rock containing 76 per cent tricalcium phosphate are acidulated with 50° Bé. sulfuric acid (62.18 per cent H_2SO_4), in order to prepare ordinary superphosphate. Taking just the right amount of acid for the reaction with the phosphate, how many pounds will be required? Leaving the reactions with calcium fluoride and calcium carbonate out of account, and assuming that there remains a moisture content of 2.3 per cent, what will be the weight of the produced superphosphate? The new compounds formed are $CaH_4(PO_4)_2 \cdot H_2O$ and $CaSO_4 \cdot 2H_2O$.

2. What is the percentage of P_2O_5 in the rock described in Problem 1? Making the assumption again that the reaction runs as the theory requires, what is the percentage of P_2O_5 present as water-soluble phosphate in the finished product? What would it be, if you started with 100 per cent tricalcium phosphate?

3. A shipment of 87 tons of Florida land pebble phosphate contains 34.96 per cent P_2O_5 in the form of tricalcium phosphate, and 3.92 per cent F in the form of calcium fluoride. The limestone impurity is 7.7 per cent, and the remainder is clay, silica and moisture. What is the composition of the rock, as far as this information indicates it? What is the exact amount of 50° Bé. sulfuric acid which will be required, all reactions proceeding as required by the theory? How much gypsum will be formed in all? Let all the fluorine escape as HF, how much hydrofluoric acid in the form of 60 per cent acid will be collectable, in pounds? What is the weight of carbon dioxide evolved, and how much will the final product weigh, moisture to be again 2.3 per cent?

4. Sulfuric acid of 30° Bé. strength (34.63 per cent H_2SO_4) is to be used for making 9 tons of 40 per cent phosphoric acid (H_3PO_4), equivalent to a 29 per cent P_2O_5 content (1.254 sp. gr.). A low-grade calcined rock with 27.6 per cent P_2O_5 content is used. How much sulfuric acid will be required, and how much rock? How many gallons of 40 per cent phosphoric acid will be obtained? The yield must be taken as 88 per cent.

5. A shaft furnace produces 47 tons of 85 per cent phosphoric acid (H_3PO_4) per day. The coke required is 2.36 pounds per pound of P_2O_5 produced. How much coke is required per day? The yield is 80 per cent over all; how much 75 per cent tricalcium phosphate rock will be needed? If all the phosphorus pentoxide produced in the yield was first collected as yellow phosphorus, how many pounds were there?

6. The 7000 pounds of soda ash under trisodium phosphate (*see* text) are made into disodium phosphate, without additions. How many pounds are obtained (in solution), and how many pounds of 45 per cent P_2O_5 phosphoric acid were required? How many pounds of 98.6 per cent NaOH must be added to form the trisodium phosphate, assuming perfect recovery? If the product crystallizes with $12H_2O$, how many

pounds are obtained, and what is the percentage of sodium phosphate in the crystals?

7. One-half ounce of baking powder of Formula (2) will generate what weight of CO_2, and what volume will the gas have at room temperature?

Reading References

"Thermal production of phosphoric acid," B. G. Klugh, *Ind. Eng. Chem.*, 24, 371 (1932).

"Ratio of fluorine to phosphoric acid in phosphate rock," D. S. Reynolds, K. D. Jacob and W. L. Hill, *Ind. Eng. Chem.*, 21, 1253 (1929).

"Fluorine, its effect on plant growth and its relation to the availability to plants of phosphorus in phosphate rocks," R. P. Bartholomew, *Soil Science*, 40, 203 (1935).

"Availability of phosphate rocks in soils of varying degrees of acidity," R. P. Bartholomew, *J. Am. Soc. Agron.*, 29, 293 (1937).

"Present status and future possibilities of volatilization process for phosphoric acid production," William H. Waggaman, *Ind. Eng. Chem.*, 24, 983 (1932).

"Thermal efficiency of the phosphate blast furnace," P. H. Royster and J. W. Turrentine, *Ind. Eng. Chem.*, 24, 223 (1932).

"Trisodium phosphate—its manufacture and use," Foster D. Snell, *Ind. Eng. Chem.*, 23, 471 (1931), with a flow-sheet.

"Phosphoric acid, phosphates and phosphatic fertilizers," Wm. H. Waggaman, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1927.

"Development and use of baking powder and baking chemicals," L. H. Bailey, *U. S. Dept. Agric. Circ.* No. 138.

"The calcination or enrichment of phosphate rock," C. G. Memminger, W. H. Waggaman and W. T. Whitney, *Ind. Eng. Chem.*, 22, 443 (1930).

"Manufacture of phosphoric acid by the blast furnace method," Henry W. Easterwood, *Trans. Am. Inst. Chem. Eng.*, 29, 1 (1933).

"The manufacture of phosphoric acid by the electric furnace method," Harry A. Curtis, *Trans. Am. Inst. Chem. Eng.*, 31, 278-292 (1935) with an isometric flowsheet of the fertilizer works.

"Superphosphate, its history and manufacture," Walter C. T. Packard, *Chemical Age*, 36, 917 (1937). The same paper: *Tr. Inst. Chem. Eng.* (London), 15, 21 (1937).

"Electrostatic separation scores advance in phosphate recovery," H. B. Johnson, *Eng. Min. Journal*, 142, 35 (1941).

"Mineral deposit," Waldemar Lindgren, New York, McGraw-Hill Book Company, 1933.

"Processing Tennessee phosphate rock at Monsanto's plant near Columbia," W. E. Trauffer, *Pit and Quarry*, 32, 24 (1940).

"Phosphate deposits of the world," George R. Mansfield, *Ind. Eng. Chem.*, 34, 9 (1942), followed by six other articles dealing with phosphates.

"The phosphate resources of Tennessee," Richard W. Smith and Geo. L. Whitlatch, Division of Geology, Bulletin 48.

"Fused tricalcium phosphate, production by defluorination of rock phosphate in a shaft furnace," T. P. Hignett and T. N. Hubbuch, *Ind. Eng. Chem.*, 38, 1208 (1946).

"Mining and processing of phosphate," *Westinghouse Engineer*, 6, 111 (1946).

"Superphosphate manufacture; a new continuous process," *Chem. Age (London)*, 54, 691 (1946).

"Phosphate fertilizer by olivine-phosphate fusion," *Chem. Eng. Progress*, 43, 163 (1947).

"Phosphorus combustion system," L. H. Almond and H. K. Steinbiss, *Chem. Eng.* 54, 105 (Oct. 1948), a graphite combustion chamber.

"Development of blast-furnace process for production of phosphoric acid," T. P. Hignett, *Chem. Eng. Progress*, 44, Part I, 753; Part II, 821; Part III, 895 (1948).

The knowledge of the requirements of vegetation rests on chemical science; on this knowledge in turn depends the choice of fertilizing agents. A considerable part of the fertilizers used are produced, or at least modified, by industrial chemical operations. With the aid of commercial fertilizers, the productivity of a given area may be raised, and a greater number of people may be supported by its yield.

Chapter 8

Fertilizers, Mixed Fertilizers, Potassium Salts, Natural Organic Fertilizers, Synthetic Urea

The greater part of the food supply of the human race comes from the soil, in the form of vegetables and grains, or of meat from domestic animals fed on the products of the cultivated soil. Plants need the following substances for their growth: water, nitrogen compounds, phosphorus compounds, and potassium compounds, in fair quantities; lime, iron, magnesium and sulfur compounds in small quantities. The observation that soils become exhausted by successive crops was made many centuries ago; in order to prevent this exhaustion the ancients allowed a field to "lie fallow" every third season. During that period the particles of rock in the soil weathered and became soluble, furnishing an extra amount of plant food which was ready for use in the succeeding season. Potassium from the feldspars and, to a lesser extent, phosphates from the phosphate rocks, were thus accumulated in the soil; the same process goes on today. The ancients also knew the use of manure and the fact that to plant certain grasses and plow them into the soil enriched it. Manure is still used, and crops of clover are grown and plowed under in order to enrich the soil with nitrogen compounds. Wood ashes were used, and supplied, as is now known, potassium carbonate. Thus the merit of modern fertilizing science is not that it has discovered the process, but rather that it has explained it. The particular elements furnished by manure, wood ashes, and clover are known, and supplies of the necessary plant foods are furnished by mines and factories in almost limitless quantities.

In stable manure, the nitrogen compounds are chiefly urea, $NH_2 \cdot CO \cdot NH_2$, and ammonium salts; at the same time manure supplies organic materials which form the "humus" which every fertile soil contains. Manure is a by-product of the farm and need not be purchased; hence its general use. It is supplemented by nitrogenous compounds from various sources, such as: ammonium sulfate from ammonia recovered during the distillation of coal, or made from synthetic ammonia; synthetic urea; sodium nitrate from Chile, or synthetic; calcium and other nitrates made by nitric acid resulting from the oxidation of synthetic ammonia; calcium cyanamide. The manufacture or method of extraction of these substances is discussed under the appropriate headings. Other important sources of nitrogen in suitable compound form are dried blood (13 per cent N), tankage (from garbage), sewage disposal sludge, bone meal, dried albumen, dried fish scraps, oil meal such as

pressed cottonseed meal which for one reason or another cannot be used as cattle food, and a number of other materials of animal origin.

Phosphorus is applied in various forms. Finely powdered phosphate rock is applied directly,[1] to the extent, for example, of 411,543 tons in 1945, eight times as much as was applied in 1929; it is insoluble in water, but weathers fast. Superphosphate with 16 to 18 per cent P_2O_5 is used to a far greater extent; its phosphate is soluble, and therefore of immediate service to the plant. Triple superphosphate, with 45 per cent P_2O_5 is gradually coming into use.

The effect of fluorine on the efficacy of phosphate materials has been studied.[2]

The slag from the Thomas and Gilchrist process[3] contains calcium phosphate, which is insoluble in water, but which weathers more readily than the tricalcium phosphate in phosphate rock; it is applied directly to the soil, after powdering. The content of iron is high (7 to 10 per cent iron oxides), but does not interfere with the fertilizing properties. The slag is very hard and must be powdered in a special ball mill with hard steel balls. Slag phosphate in the form of finely ground open hearth slag from at least one plant in the United States finds a ready market as a fertilizer; it contains 8 per cent P_2O_5. In Europe slag phosphate has been used in the fields for many years.

Precipitated tricalcium phosphate is absorbed by the plant more rapidly than the rock phosphate; a very finely divided tricalcium salt is the "colloidal phosphate" from Florida.[1] Another important material supplying phosphorus is bone meal.

Potassium salts, chiefly the chloride, are obtained from deposits in the earth, from brine ponds in arid regions, and other sources, as fully discussed in this chapter; they are sold in various grades or strengths, reported on the basis of potassium oxide K_2O, a convenient way to rate them.

Mixed fertilizers contain nitrogen as nitrates, urea, ammonium salts or other nitrogen-containing compounds; phosphorus as superphosphate, and potassium salts, chloride or sulfate; the order given above is the one generally used, so that a 2-8-2 fertilizer would contain 2 per cent nitrogen, 8 per cent phosphoric acid anhydride (P_2O_5), and 2 per cent potassium oxide, K_2O. The formulas differ for the several crops: for late potatoes, 4-8-10; wheat, 2-12-6; sugar beets, 4-12-6; clover, 0-12-15; strawberries, 5-8-7. This method of evaluation in terms of nitrogen, phosphoric acid, and potassium oxide is merely for convenience; the compounds actually present are those given above. Sodium nitrate may be mixed with superphosphate, or applied by itself. The mixed fertilizer usually contains some inert material, such as earth or gypsum; the function of the latter is mainly to dilute, but also to act as a drier, preventing caking of the powder.

The mixing of "complete" fertilizers is done in a revolving mixer not unlike a cement mixer, or in any other suitable type of mixer. The several

[1] K. D. Jacob, *Ind. Eng. Chem.*, 23, 15 (1931); *see also* Chapter 7.

[2] "Fluorine; its effect on plant growth and its relation to the availability to plants of phosphorus in phosphate rocks," by R. P. Bartholomew, Arkansas Agric. Exp. Station, *Soil Science*, 40, 203 (1935).

[3] Chapter 48.

ingredients are dumped (horse-drawn cart) into a hopper; a bucket elevator feeds the mixer. The batches are of several tons each.

The complete fertilizers refer to nitrogen, phosphoric acid (as P_2O_5) and potassium oxide; but although these three elements are the most important, it may be mentioned that eleven elements are required for successful growth of plants: phosphorus, nitrogen, potassium, calcium, sulfur, magnesium, iron, boron, carbon (in large part from the atmosphere), hydrogen, and oxygen.

The fertilizing values may be concentrated by manufacturing, for example, ammonium phosphate, which would contain both nitrogen and phosphoric acid, or potassium nitrate, containing potassium and nitrogen. For long shipment, high concentrations are desirable, since the freight on inert matter is saved. The wider use of concentrated fertilizers promises to be the next great development in this field.

Ammoniated Superphosphates. There has come into prominence of late the method of spraying a very strong ammonia, as for example a hydrous ammonia with 40 to 80 per cent NH_3, onto a charge of superphosphate contained in a revolving mixer, so that new surfaces are continually exposed. The relation may be 5 parts of NH_3 to each 100 parts of superphosphate (18 per cent P_2O_5). The ammoniated superphosphate has an increased value; also any residual sulfuric acid is neutralized, and the "rotting" of the bags from that cause is avoided. A mixed fertilizer may also be ammoniated by means of very concentrated hydrous ammonia, delivered from a steel pressure tank similar to the anhydrous ammonia containers. For example: superphosphate 900 pounds, sulfate of ammonia 52 pounds, manure salts 267 pounds, filler (sand) 673 pounds (total 1892 pounds) may be treated with 108 pounds of NH_3 in the form of 40 to 80 per cent hydrous ammonia. The anhydrous material is rarely used, for a certain quantity of water seems to be necessary to produce the essential grain structure, and avoid the undesirable powder structure which anhydrous ammonia brings about.[4] This development is a result of the decreased price of ammonia, from the 25 cent level of 20 years ago to below 6 cents a pound.

As a logical extension of this practice a urea-containing ammonia liquor has been on the market since 1932 and has found increasing favor; it contains 15.1 per cent nitrogen in the form of urea, and 30.4 per cent as ammonia (NH_3), with a total of 45.5 per cent nitrogen. Rivaling this is the sodium nitrate-containing ammonia liquor with a total nitrogen content of 44.4 per cent, and ammonium nitrate in ammonia liquor, with a total of 37.5 per cent.[5] About 180 pounds of the urea-ammonia liquor and 400 pounds of the ammonium nitrate-ammonia liquor can be added to a ton of superphosphate without causing reversion.

The ammoniation of superphosphates in this way has been a distinct advance in the science of fertilizer manufacture.

[4] U. S. Patent 2,060,310.

[5] Compare p. 57, report 114, U. S. Tariff Commission, Washington, 1937; also booklets "Urea-ammonia Liquor-A" (1933) and "UAL-B," (1936) Du Pont Company, Ammonia Department, Wilmington, Del.

The production of ammonium nitrate in the original solution, expressed in terms of 100 per cent NH_4NO_3, was 724,899 short tons in 1946. Ammonium nitrate for fertilizer purposes is shipped over both short and long distances in the solid state; under certain conditions, of heat, confinement and probably in the presence of organic impurities, it may explode. The disaster at Texas City early in 1947 started with the explosion of ammonium nitrate on board a ship in the harbor.

An interesting and safe way of transporting ammonium nitrate is in the form of Nitraprills—small shapes produced by dropping the hot concentrated solution down a tower swept by an upward flow of air.[6] The product is conditioned with diatomaceous earth, and is shipped all over the world.

TABLE 24.—*U. S. Agricultural consumption of commercial nitrogen, expressed as such, by kind of material, for the crop year 1947-48.**

	Short tons
Sulfate of ammonia	185,000
Ammonium nitrate	175,000
Ammoniating solutions	250,000
Nitrate of soda	130,000
Calcium nitrate	1,600
Calcium cyanamide	15,600
Ammonium phosphates	32,600
Urea and calurea	7,500
Organics	30,000
All materials	827,300

* *Chem. Eng.*, 55, 115 (1948).

Sodium Nitrate Solid Pellets. It has been found advisable to alter the condition of Chilean nitrate intended for fertilizer mixing, by forming it into round pellets, in order to remove its hygroscopic property. The method[7] consists of melting the nitrate at the temperature of not over 350° C. [662° F.], forcing it through a filtering screen, and spraying it into a cooling chamber; this gives a product consisting of small balls with a hard outer surface, and solid throughout. Another method[8] provides for the incorporation of 5 per cent of potassium nitrate, magnesium nitrate or ammonium sulfate, giving again a non-hygroscopic, solid, hard pellet, well suited to the agricultural drill which applies the mixed fertilizer to the soil. This improvement has been carried over into synthetic nitrate manufacture. Furthermore, ammonium nitrate in pellet form is available.[9]

POTASSIUM SALTS

The most extensive mineral deposits of soluble potassium salts are those at Stassfurt, in Germany, which supplied nearly all the world's requirements until 1914. Since the end of World War I, the deposits in upper Alsace, near Mulhouse, have been developed until they yield about one-third of the Stassfurt tonnage; they are similar in nature to the

[6] *Chem. Eng.*, 55, 99 (1948).
[7] U. S. Patent 1,937,757.
[8] U. S. Patent 2,021,927.
[9] U. S. Patent 2,402,192.

German deposits. A third deposit of similar character lies in Poland, near Kalusz in the southeastern part, and yielded 261,310 tons of potassium salts of all grades in 1931. The German production was about 1½ million tons for that year. A fourth producing deposit is the one in Carlsbad, New Mexico, which began shipments in 1931, and produced 1,354,187 short tons of merchantable salts in 1945.

The Stassfurt area lies in the central part of Germany, between Magdeburg and Halle. The deposits of the potash beds are at a depth of about 1000 feet, and overlie a bed of salt (NaCl) 3000 feet thick. Over the potash beds a layer of clay separates them from another deposit of salt (NaCl) of more recent geological origin. Three potash layers are distinguished, of which the upper is 300 feet thick and extends over many square miles; it consists of carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$ (40%), mixed with salt (20%) and other impurities. Below the carnallite lies polyhalite, $2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$, and below this, kainite, $MgSO_4 \cdot KCl \cdot 3H_2O$. The geological history of these deposits is that salt deposited from sea water leaving a mother liquor which gradually gained in potassium salt content; a change in the topography caused the isolation of the bay, and the lake so formed dried completely; it was during this dry period that the potassium salts deposited. A similar relation of solubilities is exhibited by present-day sea water, which is evaporated for salt in the south of France: after the salt has deposited, the more soluble magnesium salts with some potassium remain in the mother liquor, and are run off because the magnesium is bitter.

The method of mining at Stassfurt is by shafts and tunnels. The mineral is dislodged by blasting with black powder; it is loaded in mine cars and hauled to the refining plant at the mouth of the shaft.

The German potash salts for fertilizer purposes are produced in four grades. Their value is based largely on the calculated potassium oxide equivalent: kainite, with 12 per cent K_2O; manure salts, with 20 per cent; potassium chloride, with 50 per cent; potassium sulfate, also with 50 per cent.

The crude carnallite is refined to potassium chloride by treating the crushed material with a hot solution of 20 per cent magnesium chloride, from a previous operation. In this solution, the salt (NaCl) is insoluble, and is left behind with calcium sulfate and other impurities; from this solution, potassium chloride deposits on cooling. The mother liquor is concentrated and gives on cooling a lower grade of potassium chloride utilized as manure salts. The first crop of potassium chloride may be refined further by washing with cold water; this further treatment is applied only to limited quantity.[10]

The Alsatian deposits [11] consist of two strata. The upper one is about 3 feet thick, and contains 35 to 40 per cent potassium chloride; the depth is 1500 feet below the surface in one section, but greater in others. The

[10] To the north and northwest of the Stassfurt basin potassium salts are also found, in Hannover, Braunschweig and Mecklenburg; these deposits are smaller, and consist chiefly of sylvine or sylvinite, KCl·NaCl, more or less pure.

[11] "The Alsatian potash industry," Henri Vigneron, *Chem. Met. Eng.*, 24, 655 (1921), with 16 illustrations.

lower layer is 7.5 to 16 feet in thickness, and lies about 50 feet lower; it contains 24 to 32 per cent potassium chloride. Both layers are essentially sylvinite, $KCl \cdot NaCl$, containing sodium chloride as impurity, and clay; the purification is by crystallization, and leads to potassium chloride 98 per cent pure (or with 61 per cent K_2O content). Lower grades are obtained from mother liquors; a part of the mine product is shipped after mere crushing. The grades marketed are: sylvinite, 12 to 16 per cent K_2O; sylvinite rich, 20 to 22 per cent or 30 to 32 per cent; potassium salt (*sel de potasse*), 40 to 42 per cent; and potassium chloride (*chlorure de potasse*), 62 per cent K_2O. The first two are crushed mineral; the last two have been concentrated by solution and crystallization.

The American deposits lie in the southeastern part of New Mexico, in Eddy and Lea counties, and in the neighboring counties in Texas, Loving, Winkler, Ector, Crane, Upton, Reagan and Crocket. (*See* Fig. 56.) The

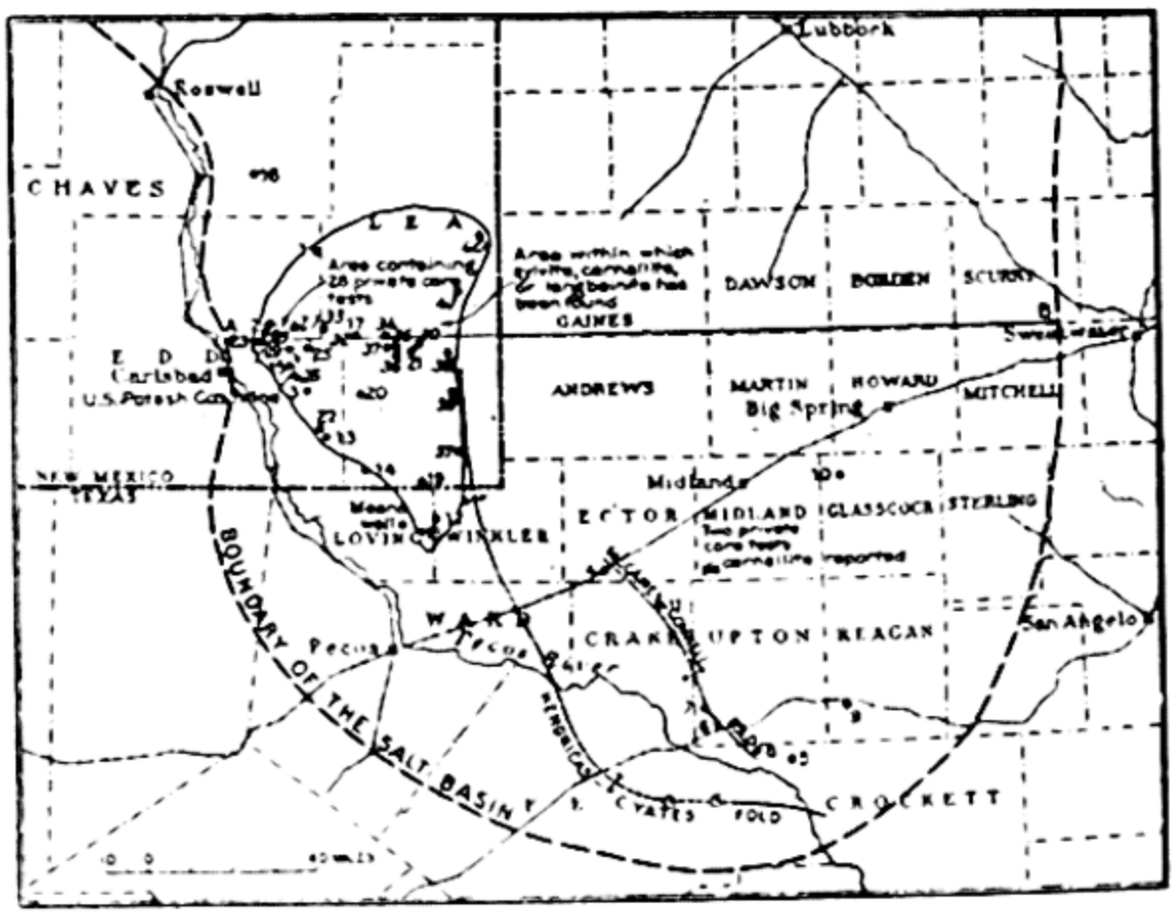


FIGURE 56.—Map of the Permian potash field in Texas and New Mexico. (Courtesy of the Department of the Interior, U. S. Geological Survey.) The dots and numerals mark test drilling locations.

deposits are of the Permian geologic age. The area covers underground deposits of rich potassium salts, chiefly chloride; in Eddy County, there are ten beds at depths between 800 and 1762 feet below the surface, varying in thickness from 1 foot 2 inches to 4 feet 6 inches, and having an arithmetical total of 36 feet. (*See* Fig. 48.) The potassium minerals are sylvinite (the richest), kainite, and some polyhalite. At a depth of 1267 feet, the bed is 3 feet 6 inches of sylvinite; at 1311 feet another deposit of 3 feet occurs, consisting of sylvinite and polyhalite; while at 1365 feet depth, a 2-feet thick bed of sylvinite is available. A shaft sunk near Carlsbad, New Mexico, serves a mine operating since 1931; in that year, a large tonnage was produced, with a content of 25.6 per cent K_2O. The mineral was higher in potash than the test cores had indicated.

In addition, there are numerous beds of polyhalite, an impure potassium sulfate, averaging close to 10 per cent K_2O, at depths of 1100 to 2752 feet.[12] The thickest bed is 15 feet 6 inches, at a depth of 1459 feet, with 8.8 per cent

[12] Regarding the possible exploitation of the polyhalite beds, it might be noted that potassium in the form of the sulfate is the preferred form for the fertilization of the citrus fruit crop. H. H. Storch, *Ind. Eng. Chem.*, 22, 934 (1930); Everett P. Partridge, *Ind. Eng. Chem.*, 24, 896 (1932).

K_2O, in Eddy County. The deepest is in Winkler County, Texas, where at 2267 feet depth, a bed of 9 feet 8 inches occurs, with 7.23 per cent K_2O, and just over it, at 2257 feet, is a layer 6 feet thick, with 10.63 per cent K_2O. The richer mineral tapped by the Carlsbad shaft has not been found in the Texas counties.

A refinery has been erected at Carlsbad, N. M. (Potash Company of America) in which a flotation method is used for the separation of potassium chloride from its valueless companion in sylvinite, sodium chloride. The production is near 100,000 tons of KCl, with 60 per cent K_2O.

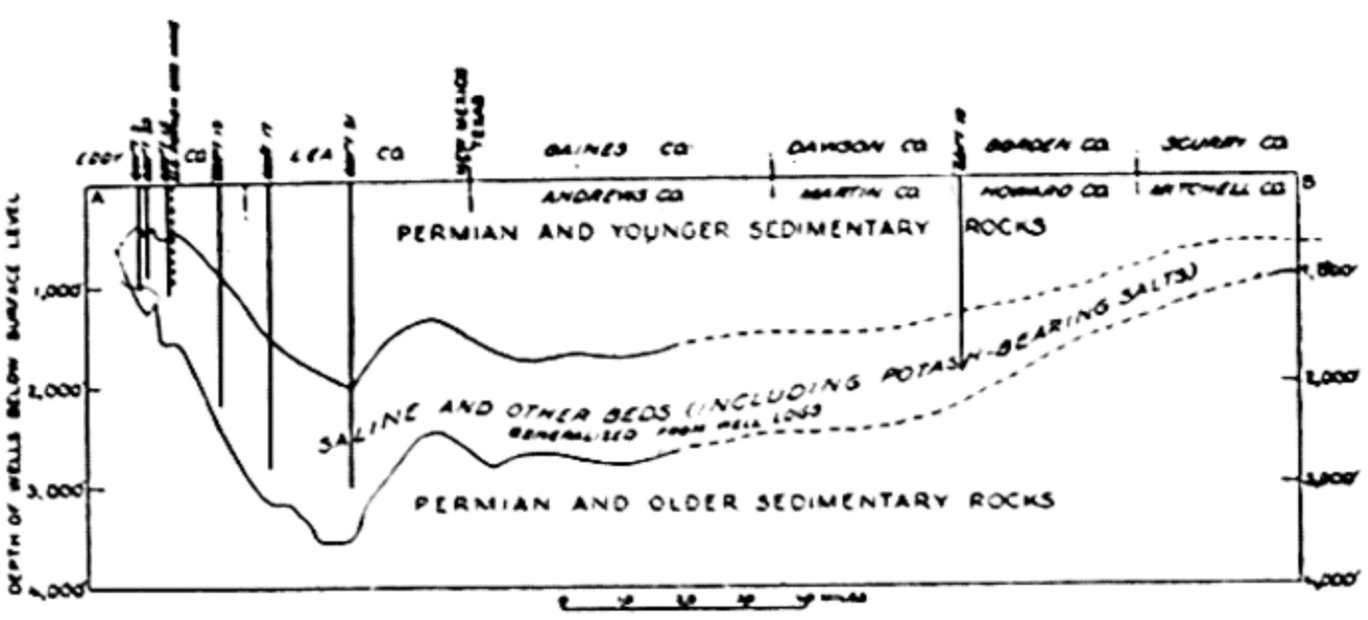


FIGURE 57. — Projected section of Permian potash field in Texas and New Mexico. (Department of the Interior, U. S. Geological Survey.)

The New Mexico and Texas deposits were probed during and since the war of 1914-18, by private citizens and by government agencies. The Mulhouse deposits are due solely to private enterprise; they were discovered while searching for petroleum, before 1914.

Potassium Salts from Brines. Besides the important deposits of Stassfurt, of the East of France, of southeastern Poland, of New Mexico and Texas, brines from certain lakes in dry areas constitute a source of potassium salts. Of the several enterprises begun within the United States during World War I to relieve the shortage resulting from the blockade of the German seaports, only one has survived, that of the American Trona Company [13] at Searles Lake, in the desert between California and Nevada. This "lake" is really a deposit of solid salts permeated by a brine.[14] The salts are stiff enough to carry a dirt road. From a depth of 70 feet below the surface of the lake, the brine is pumped to the large modern plant

[13] Now the American Potash and Chemical Corporation, Trona, Cal.

[14] Composition of Searles Lake Brine:

NaCl	16.35	Per cent by weight
Na_2SO_4	6.96	
KCl	4.75	
Na_2CO_3	4.74	
*$Na_2B_4O_7$	1.51	
†Na_3PO_4	0.155	
NaBr	0.109	
Miscellaneous	0.076	
Total Solids	34.65	
Water by diff.	65.35	

The American Potash and Chemical Corporation uses vacuum crystallization extensively (see Perry, "Chemical Engineers Handbook," p. 1486), saving space, circulating water, and material in process.

* Equiv. to 2.86 per cent $Na_2B_4O_7 \cdot 10H_2O$.

† Equiv. to 0.067 per cent P_2O_5.

situated on the shore four miles away, where it is mixed with end liquors from various plant operations, and concentrated in triple-effect evaporators, which are 86 feet high. The flow of steam through the evaporators is counter to the flow of brine, so that the strongest brine is at the highest tem-

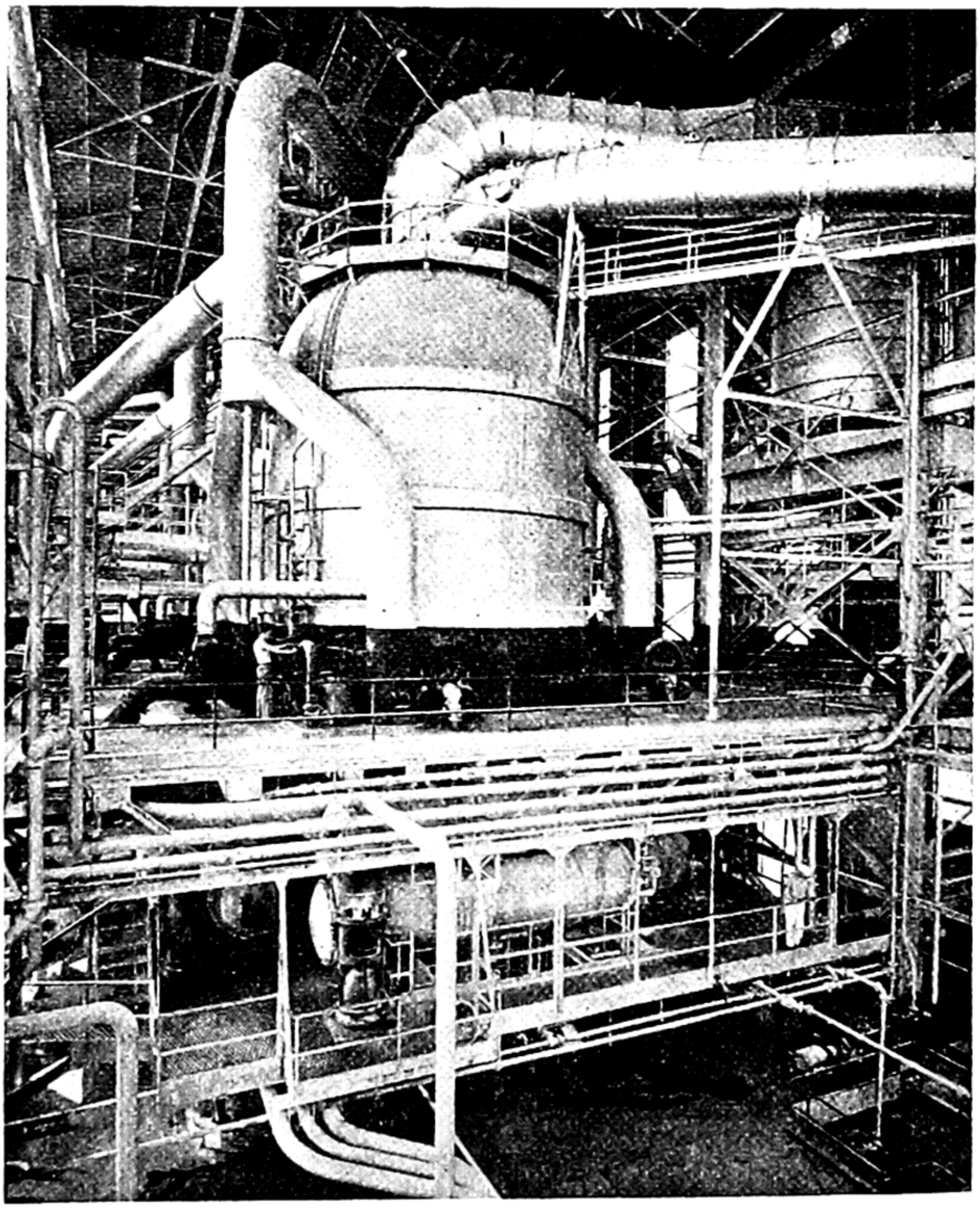


FIGURE 58.—One of the large triple-effect evaporator units of the Trona plant of the American Potash and Chemical Corporation, Trona, California. (By permission.)

perature; thus potassium chloride and borax are retained in solution, even as their concentration rises, because they are more soluble at the higher temperature. During the evaporation, much of the salt (NaCl), mixed with sodium carbonate and sodium sulfate, separates out and is continuously removed from the evaporators. The concentrated liquor, essentially saturated with potassium chloride, is cooled to 100° F. in vacuum crystallizers, in three stages; the potassium chloride deposits in these and, after discharge from the crystallizing vessel, is collected and removed by treatment in

continuous thickeners. After centrifuging and drying, this salt is ready for shipment. The mother liquor is cooled to about 80° F., at which point the crude borax separates out. It is dissolved in hot water, filtered, and crystallized in pure form by controlled cooling in vacuum crystallizers.

The main products are potassium chloride and borax, about twice as much of the former as of the latter. For example, in 1946, 212,000 tons of potash salts, and 102,148 tons of borax were produced.

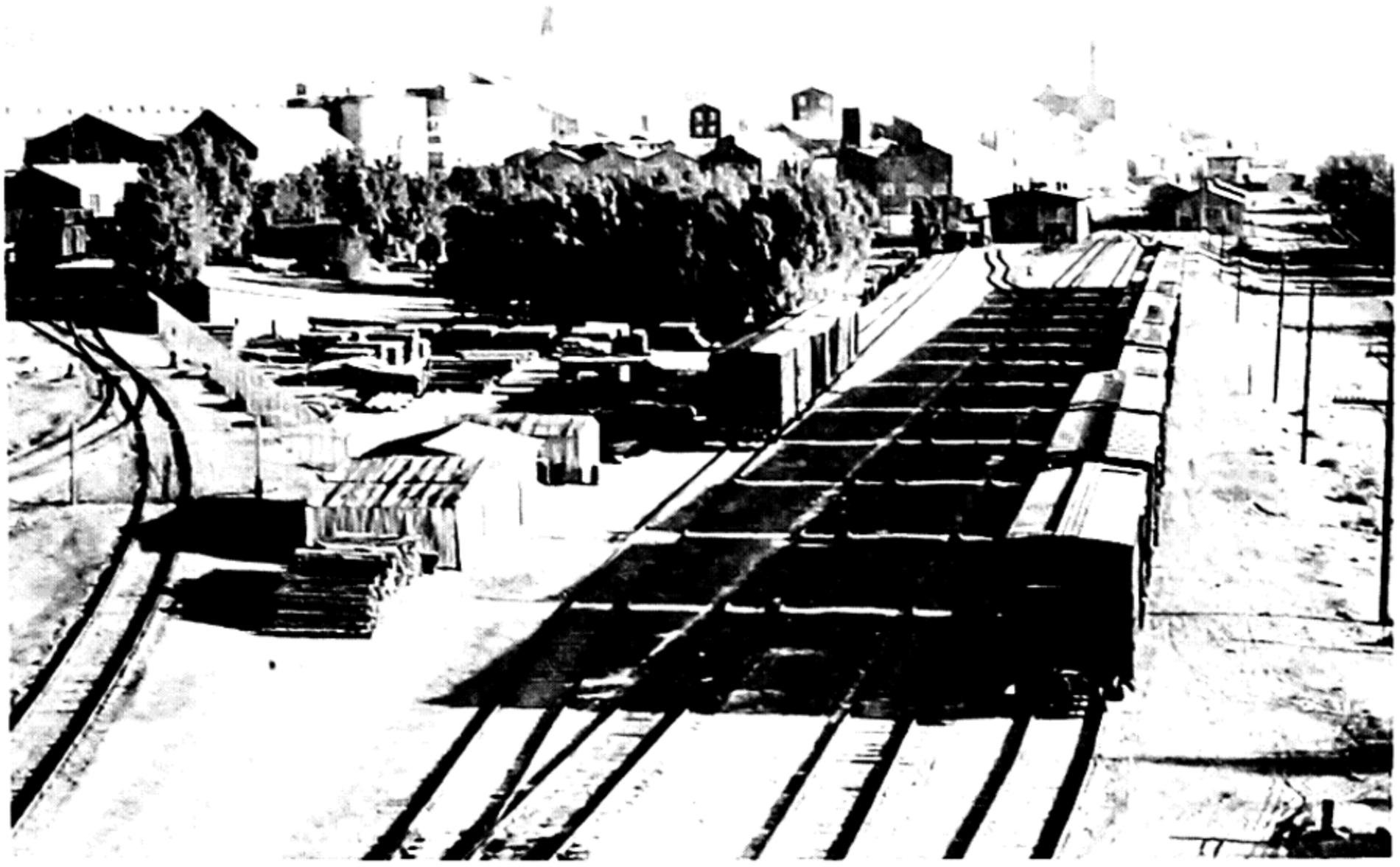


FIGURE 59.—View of the Trona plant of the American Potash and Chemical Corporation, California. Searles Lake is in the immediate background. (Courtesy of the American Potash and Chemical Corporation.)

The sodium chloride deposit formed during the evaporation contains sodium carbonate and sodium sulfate, which are removed from the evaporation cycle by filtration and processed to produce natural soda ash and natural salt cake. In 1946, there were produced at Trona 86,266 tons of natural soda ash and 139,686 tons of natural salt cake.

Lithium phosphate is recovered in the soda ash and salt cake process; it is separated from burkeite (sodium carbonate-sodium sulfate double salt) by pneumatic flotation as lithium sodium phosphate, with ordinary stove oil as the flotation agent.[15]

Other products from the Searles Lake brine include "Pyrobor," dehydrated borax, potassium sulfate, boric acid and bromine. The total 1946 production for all Trona chemical products was 541,327 tons.

Before the developments at Searles Lake, the bulk of the world's borax was produced from colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$, by decomposing it with a boiling sodium carbonate solution, filtering and crystallizing. The production at

[15] "Lithium from Searles Lake," W. A. Gale, *Chem. Ind.* (September, 1945).

Searles Lake of not only borax but muriate of potash and many by-products made it possible to obtain borax more cheaply than from colemanite. Since then, however, extensive deposits of rasorite, $Na_2B_4O_7 \cdot 4H_2O$, have been discovered near Kramer, California, which are now mined. The ore is shipped to Los Angeles harbor, dissolved in water under heat and pressure, strained, filtered and crystallized as pure borax, $Na_2B_4O_7 \cdot 10H_2O$.[16]

Boric acid, HBO_3, a white solid, is made by treating borax with sulfuric acid. A technical grade and a U.S.P. grade are made, and the latter is available in the form of flat crystals, or as a powder.

The U. S. production of crude borates from all sources was 325,935 short tons in 1945. Borax of technical grade, in bulk (carload lots) was quoted at $44.50 a ton in May, 1948.

A brine from a drying salt lake near Zarsis in Tunis has become the basis of a growing industry. The active exploitation of the brine in the Dead Sea [17] is continuing; the production of potash salts in 1942 (the best year) was 104,200 metric tons, with a K_2O content of 52,100 metric tons.

Other mineral sources of potassium are the following: Alunite, $K_2Al_6(OH)_{12}(SO_4)_4$, was mined for three years during World War I and worked for potassium sulfate, in Sulphur, Nevada, and Marysvale, Utah. Leucite, $(KNa)AlSi_2O_6$, is successfully worked for potassium in Italy by means of hydrochloric acid. Greensand of New Jersey (Odessa, Del.), shales in Wyoming and other states, and feldspar also contain potassium. The nitrate deposits of Chile contain potassium, and there is now recovered a 25 per cent KNO_3 material, by means of the Guggenheim process; in case of necessity, this method could be applied to all the Chile nitrate produced, and with normal production, approximately 300,000 tons a year of potassium nitrate could be obtained. Other deposits are in Spain, Abyssinia, Canada and Russia (Solikamsk).

Until World War I, the United States had imported all or nearly all its potash salts. Beginning with the 1914-18 period, domestic sources were actively sought and vigorously developed. In 1935, 76.4 per cent of the world production of potassium salts from minerals or brines was the Stassfurt-Mulhouse one, and of that production, the United States imported 13.9 per cent. During World War II, all (or nearly all) the potash needed for agriculture and industry was supplied from domestic sources; since 1940, the exports have exceeded the imports of fertilizer potash by 37,000 tons or more. In 1946, after meeting the needs of agriculture and industry, 46,000 tons were available of potassium salts for export.[18]

Aside from minerals and brines, potassium salts are obtained by collecting the flue dust which passes out of cement kilns,[19] by means of a Cottrell precipitator; it is estimated that 2 to 5 lbs. of K_2O may be recovered for

[16] *Chem. Met. Eng.*, 42, 430 (Aug., 1935).

[17] "The Dead Sea: a storehouse of chemicals," M. A. Novomeysky, *Trans. Inst. Chem. Eng. (London)*, 14, 60 (1936). In the partition of Palestine proposed in 1947 by the United Nations, the Dead Sea would be bordered by three countries: the Arab Palestine, Trans-Jordan and the State of Israel.

[18] "Plant food in the U. S.," A. L. Mehring and K. G. Clark, *Agricultural Chemicals* (September, 1947).

[19] *Ind. Eng. Chem.*, 10, 834 (1918).

each barrel of cement made. For iron blast furnaces, similar installations indicate that 17 lbs. of K_2O may be conserved for each ton of pig iron manufactured. The ashes from fermented molasses residues, ashes from the spent pulp of the sugar beet (7000 tons yearly), wool washings, and kelp [19] are commercial sources of potassium compounds.

Potassium nitrate may be used for fertilizing; it has the advantage of combining two of the essential elements. Formerly the extraction of potassium nitrate from the upper layer of the soil near stables was of some importance (India); the constant re-formation of nitrate is due to the growth of bacteria. Potassium nitrate may be made by double decomposition of potassium chloride with sodium nitrate:

$$KCl + NaNO_3 \rightarrow KNO_3 + NaCl.$$

Solid potassium chloride is added to a strong hot solution of sodium nitrate; sodium chloride first separates; then on cooling, potassium nitrate crystallizes. Another method is to pass nitrogen peroxide into a potassium chloride solution.[20]

In the Kooban province in southern Russia, extensive plantations of sunflowers furnish stalks which are ashed and then extracted for potash; the production is over 20,000 tons a year.[21]

Potassium salts are also in demand in the chemical industries, because they crystallize well as a rule, whereas sodium salts do not. As a result, it is easier to separate potassium compounds from other reaction products than to separate the corresponding sodium compounds. Purification by crystallization is also easier for potassium compounds than for sodium compounds. Examples of potassium salts manufactured on an industrial scale in preference to the sodium salts merely because the former crystallize with ease, are potassium permanganate, dichromate, chlorate, and ferricyanide. In some cases, the potassium compound is preferred because the corresponding sodium compound is hygroscopic; in still others, because of the specific action of potassium, which differs from that of sodium.

TABLE 25.—*World production of potash minerals, in metric tons.**

	1944		1945	
	Production	K_2O Equivalent	Production	K_2O Equivalent
U. S., potassium salts	1,431,982	757,103	1,440,879	793,096
France (Alsace)	2,945,346	500,700		†
Germany, crude pot. salts	15,861,933	1,925,530		
Italy, alunite	n.r.			
Poland	n.r.			
Spain	675,836	116,000	718,700	115,000
U.S.S.R.	n.r.			
Palestine for 1943	93,750	46,900		
Australia for 1942, alunite	4,784			
India (British) for 1942, KNO_3	7,110	3,410		

* "Minerals Yearbook," 1945.
† The French potash production in 1947 was equivalent to 624,000 metric tons of K_2O.

[20] *Ind. Eng. Chem.*, 23, 1410 (1931).
[21] *Chem. Met. Eng.*, 30, 501 (1924).

World reserves are indicated by the following figures: Stassfurt, 8 billion tons K_2O; Mulhouse basin, 350 million; Dead Sea, 2 billion; U.S.S.R., very large, of the order of the Stassfurt deposits; Searles Lake, 20 million; total United States reserves, 73 million short tons.[22]

Natural Organic Fertilizers

By-products of the packing industry which are of value as fertilizers are dried blood, bone meal, and tankage. The fish industry contributes fish scrap. In a number of other industries there are by-products which serve primarily as cattle feed, but if, for any reason, they are unacceptable for that purpose, they may be of value as fertilizing agents.

In the slaughter house, the blood is pumped to a coagulating tank with a conical bottom. It is cooked until coagulated, and of the consistency of liver. On standing a few hours, a separation takes place; water settles out at the bottom and is drawn off. The coagulum is pressed, dried, and powdered; it forms a dark, reddish meal. It is either sold as such, or mixed with potash salts and phosphates to make a rich fertilizer.

Bones are cooked in open tanks, or steamed under pressure; in either case, grease is removed. The degreased bones are crushed and powdered.

Tankage is used primarily for feeds; it is a brown meal, containing 9.5 to 11 per cent nitrogen as NH_3 and 12 to 20 per cent of bone phosphate of lime. Applied to the soil, tankage decomposes more slowly than dried blood. Fertilizer tankage is produced from meat scraps, intestines, bones, and carcasses of dead or condemned animals, by cooking under a steam pressure of 40 lbs. for 4 to 12 hours. Grease and tallow float to the surface and are removed; the solids are separated from the tank water, and ground. The tankage still contains 10 to 20 per cent grease which is generally removed by naphtha, before it is sent out as a fertilizer.

Guano is a mixture of birds' excrements and fish bones and other fish refuse, found on certain islands off the Peruvian coast, where the rainfall is slight. The deposits are surface deposits and are still in process of formation, but their importance as to tonnage has decreased. Their quality has also decreased as the materials rich in urea and ammonium oxalates are practically exhausted. Guano is found and mined in other localities.

A nitrogenous material is produced from activated sludge in sewage disposal plants; such a material is Milorganite, described in Chapter 13.

Synthetic Urea

A nitrogenous material of synthetic origin is synthetic urea $NH_2 \cdot CO. NH_2$; in solution its formula is more probably $HN{:}C\langle^{NH_3}_{O}$. Its nitrogen content is remarkably high, namely 46.6 per cent for the pure substance. Before the outbreak of World War II, it was manufactured in Germany on a large scale. Its production in the United States has grown steadily; consumption of urea in the 1947-48 crop year is expected to be 7,500 tons of

[22] "Potash reserves of the United States," Samuel H. Dolbear, a report to the American Potash Institute, Washington, D. C., 1946.

nitrogen. The suitability of synthetic urea as a plant food is equal to that of the natural urea in manures.

The process of Carl Bosch and Wilhelm Meiser[23] consists in passing the mixed ammonia and carbon dioxide gases, with some moisture, into an autoclave held at 130° to 140° C. (266° to 284° F.); ammonium carbamate, $NH_2 \cdot CO \cdot ONH_4$, forms first, and is transformed into urea. (Fig. 59a.)

FIGURE 59a.—Synthetic urea storage pile, at the Leuna Works, Germany. (Bourke-White Photo from Pictures, Inc., New York.)

$$2NH_3 + CO_2 \rightleftharpoons \underset{\substack{ammonium\\carbamate}}{NH_2 . CO . ONH_4}; \text{ and then,}$$

$$NH_2 . CO . ONH_4 \rightleftharpoons \underset{urea}{NH_2 . CO . NH_2} + H_2O.$$

The conversion is about 40 per cent, and there is discharged from the autoclave, continuously if desired, a melt which is introduced directly into a plate still. Steam enters at the base, and drives out the uncombined ammonia and carbon dioxide, while a solution of urea is discharged at the bottom of the still. It is concentrated and crystallized.

The make-up gas may be conveniently introduced by running a solution of ammonium carbamate into the upper part of the column; the gas driven out is compressed in warmed compressors and conveyed by warmed lines to the autoclave, to prevent the deposition of ammonium salts.

[23] U. S. Patent 1,429,483.

The Krase process[24] provides for the introduction of liquid ammonia and liquid carbon dioxide into an autoclave. Modifications[25] provide for neutralizing unchanged ammonia with phosphoric acid, producing a concentrated fertilizer containing two of the essential elements.

The average value per ton of all the potassium salts (1,597,160 short tons) sold in 1945 was $18.98. Muriate of potash was 53½ cents a unit ton of K_2O; hence for the 60 per cent K_2O grade, the price was $32.20 a ton, while the manure salts with 22 per cent K_2O minimum were 20 cents per unit ton. Sulfate of potash (90 to 95 per cent K_2SO_4, on the basis of 90 per cent K_2SO_4) was $36.25 a short ton.[26] A quotation in May, 1948 for domestic muriate, 60 per cent K_2O, was 37½ cents per unit ton, or $22.50 per ton of salt (Carlsbad); another was 48½ cents per unit ton, or $28.50 per ton (Trona, Cal.).

The developments in the nitrogen industries are part of a study of the general field of fertilizers; these developments have been presented in Chapter 6, and many statements and figures of primary interest to the fertilizer field are included there.

Other Patents

U. S. Patent 2,074,880, molecular addition compound of calcium sulfate and urea, $CaSO_4 \cdot 4CO(NH_2)_2$, made by reacting mixtures consisting of calcium sulfate dihydrate and urea in a saturated aqueous urea solution. The following U. S. Patents have been assigned to the Tennessee Valley Authority: 2,037,306, on manufacture of ammoniated superphosphate; 2,040,081; agglomeration of fine phosphate rock; 2,043,328; manufacture of dicalcium phosphate; 2,044,774, treating phosphate rock to eliminate fluorine. U. S. Pat. 2,402,192, agricultural ammonium nitrate in pellet form.

Problems

1. What is the highest percentage of potassium expressed as K_2O (the customary fertilizer unit for the element potassium) which any potassium chloride preparation can contain?

2. If a control laboratory found a 5-gram sample of a crude potassium sulfate to yield a precipitate of potassium chloroplatinate (K_2PtCl_6) weighing 10.00 grams, what is the potassium content of the original sample in terms of K_2O, and what is the percentage of potassium sulfate in the sample?

3. One hundred tons of mineral containing 59 per cent of carnallite pass through the refinery and are made into crude potassium chloride containing 48 per cent K_2O. If the recovery is 72 per cent, how many tons of crude potassium chloride will be obtained?

4. Fixed nitrogen in the form of 96 per cent urea totaling 1000 metric tons of nitrogen are ordered. How many pounds of material will have to be shipped? Make the same computation for commercial ammonium sulfate, Chilean nitrate, assuming for each 96 per cent purity.

5. 2000 pounds of rasorite carrying 85 per cent $Na_4B_2O_7 \cdot 4H_2O$, are dissolved, filtered, and run to the crystallizer as a 25 per cent solution of borax, $Na_2B_4O_7 \cdot 10H_2O$, at 150° F. After cooling to 100° F., the crystals are centrifuged and go to the drier carrying 5 per cent moisture. The mother liquor contains 8 per cent borax. What yield of dry crystals is obtained?

[24] "A direct synthetic urea process," by H. J. Krase, V. L. Gaddy, and K. G. Clark, *Ind. Eng. Chem.*, 22, 289 (1930).
[25] U. S. Patents 1,797,095; 1,782,723.
[26] "Minerals Yearbook," 1945.

Reading References

"Manufacture of Soda," 2nd ed., T. P. Hou, New York, Reinhold Publishing Corp., 1942.

"Fertilizers," T. Lyttleton Lyons, Encyclopedia Americana (8 pages).

"Phosphoric acid, phosphates and phosphatic fertilizers," Wm. H. Waggaman, New York Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1927.

"Recent developments in the preparation and use of fertilizers," William H. Ross, *Ind. Eng. Chem.*, 23, 19 (1931).

"Potash in North America," J. W. Turrentine, Reinhold Publishing Corp., 1943.

"Soilless Growth of Plants," C. Ellis and W. W. Suaney, Second Edition revised by T. Eastwood, Reinhold Publishing Corp., 1947.

"Commercial possibilities of the Texas-New Mexico potash deposits," James S. Wroth, *Bur. Mines Bull.* No. 316 (1930).

"Texas-New Mexico Polyhalite as source of potash for fertilizer," E. P. Partridge, *Ind. Eng. Chem.*, 24, 895 (1932).

"The industrial development of Searles Lake brines," John E. Teeple, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1929.

"Volatilization of potash from potassium aluminum silicates," S. L. Mardorsky, *Ind. Eng. Chem.*, 24, 233 (1932).

"The Alsatian potash industry," Henri Vigneron, *Chem. Met. Eng.*, 24, 655 (1921).

"The Alsace potash deposits," Paul Kestner, *J. Soc. Chem. Ind.*, 37, 291T (1918), with a map.

"Potash mining in Germany and France," George S. Rice and John A. Davis, Bureau of Mines Bulletin 274 (1927).

"Extraction of potash from polyhalite," H. H. Storch, *Ind. Eng. Chem.*, 22, 934 (1930).

"Extraction of potash from polyhalite, II—Production of syngenite and by-product magnesia," H. H. Storch and N. Fragen, *Ind. Eng. Chem.*, 23, 991 (1931).

"The data of geochemistry," *U. S. Geol. Survey Bull.* No. 695, F. W. Clarke, 4th ed. 1930, includes description of Stassfurt salts.

"A sulfate of ammonia plant," F. A. Ernst and W. L. Edwards, *Ind. Eng. Chem.*, 19, 768 (1927).

"Synthesis of urea," a chapter by H. J. Krase, in "Fixed Nitrogen," by H. A. Curtis, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1932.

"Urea-ammonia liquor, a new fertilizer material," F. W. Parker and F. S. Keenen. *Chem. Met. Eng.*, 39, 540 (1932).

"Progress in garbage reduction," Harrison E. Howe, *Ind. Eng. Chem.*, 19, 608 (1927).

"By-products in the packing industry," Rudolf A. Clemen, Chicago. University of Chicago Press, 1927.

"Chemical reactions in fertilizer mixtures," Frank O. Lundstrom and Colin W. Whittaker, *Ind. Eng. Chem.*, 29, 61 (1937).

"Ammoniation of double superphosphate," L. M. White, J. O. Hardesty and W. H. Ross, *Ind. Eng. Chem.*, 27, 562 (1935).

"Rate of dolomite reactions in mixed fertilizers," F. G. Keenen and W. A. Morgan, *Ind. Eng. Chem.*, 29, 197 (1937).

"Concentrated fertilizer," W. S. Landis, *Ind. Eng. Chem.*, 28, 1470 (1936).

"Fertilizer materials," Oswald Schreiner, Albert R. Merz, and B. E. Brown, in the Yearbook 1939, U. S. Department of Agriculture.

"Chemistry of the Trona Process," W. A. Gale, *Ind. Eng. Chem.*, 30, 867 (1938).

"Potassium chloride from the brine of Searles Lake," R. W. Mumford, *Ind. Eng. Chem.*, 872 (1938).

"Expansion of the Trona enterprise," plant of the American Potash and Chemical Corporation, G. Ross Robertson, *Ind. Eng. Chem.*, 34, 133 (1942).

"Bonneville potash," *Mining World*, 7, No. 9 (August, 1945), pp. 27-32, quoted through "Minerals Yearbook."

"Utah desert yields potassium chloride for Western agriculture," H. R. Smith, *Chem. Met. Eng.*, 51, 94 (Dec., 1944).

"Chemical industry development on Pacific Coast," W. Hirschkind, *Chem. Eng. Progress*, 43, 145 (1947).

"Fertilizers and lime in the U. S.," U. S. Dept. Agr., Misc. Publ. 586, 94 pages (1946), by Frank W. Parker, J. Richard Adams, K. G. Clark, K. D. Jacob and A. L. Mehring.

"Agriculture," Philip H. Groggins, *Chem. Eng.*, 55, 114 (April, 1948).

References on Soils and Fertility in general:

"Crop production and soil management," J. F. Cox, New York, John Wiley & Sons, Inc., 1925.

"Farm fertility," S. B. Haskell, New York, Harper and Brothers, 1923.

"Soil fertility and permanent agriculture," C. G. Hopkins, Boston, Ginn and Co., 1910.

"World conditions as to plant foods," C. C. Concannon, *J. Chem. Ed.*, 7 (2), 2634 (1930).

"Leucite as a source of alumina, potash, and silica," Baron Gian Alberto Blanc, *Trans. Inst. Chem. Eng.* (Brit.), 9, 49 (1931).

"The examination of soils by means of aspergillus niger," A. M. Smith and A. Dryburgh, *J. Soc. Chem. Ind.*, 53, 250T (1934).

"Soil dynamics," C. C. Nikiforoff, *Sigma Xi Quarterly*, 30, 36-65 (1942).

The manufacture of portland cement has become an important industry; in 1946, the production was 30.8 million tons, for the United States, including Puerto Rico and one mill in Hawaii. Operations at the Hawaiian mill were discontinued at the end of the year (1946). Gypsum in the same year was mined to the extent of 5.63 million tons, while the lime produced exceeded 5.9 million tons. These three industries are now recognized as essentially chemical.

Chapter 9

Portland Cement, Lime, and Gypsum Plaster

The tremendous expansion of the portland cement [1] industry in the last twenty years is due to extensive road-building programs, to the development of reinforced concrete construction, and to the adaptability and uniformity of the material. Concrete roads are permanent, and their upkeep practically nil. Reinforced concrete permits the construction, for instance, of a horizontal platform bridging the space between two walls, capable of carrying heavy loads without other support than itself. Not only walls and piers, but entire buildings are now constructed of concrete. Bridge piers, tunnels, dams, and canal walls are built of concrete as well as sidewalks, steps, garage and factory floors, and building foundations. One reason for the almost universal use of portland cement is the comparative ease of working it (pouring); another is its strength, which increases with age; a third is its uniformity, which permits calculations of strength as reliable as those made for structural steel.

Portland cement is a greenish-gray, impalpable [2] powder. Its essential constituents are lime, silica, and alumina, which are combined to form tricalcic silicate, $3CaO \cdot SiO_2$, tricalcic aluminate, $3CaO \cdot Al_2O_3$, and dicalcic silicate,[3] $2CaO \cdot SiO_2$; these are unstable compounds, which on being wetted, rearrange with different speeds. Tricalcic silicate acts rapidly, forming gelatinous calcium hydrate and gelatinous silica, and to this change is due the initial set which occurs in 3 hours; the hydration continues, the gelatinous material binding the grains of sand which are always added, and the crushed stone filler, to a hard mass. Tricalcic aluminate acts with the same rapidity as tricalcic silicate, but does not produce a strong bond. Dicalcic silicate acts only after months have elapsed.[4] The hardening of portland cement continues for years, and the concrete made from it increases in strength. As time passes, the gelatinous calcium hydrate crystallizes, adding a further element of strength.

In mixing water with portland cement and stones, to give the concrete,

[1] The name was given by Joseph Aspdin, because the cement he made in 1824 yielded stones resembling those quarried near Portland, England; his cement was the prototype of the present portland cement.

[2] No grains can be felt between the fingers.

[3] There are four forms of dicalcic silicate, all of which occur in portland cement. The major one, however, is β-$2CaO \cdot SiO_2$.

[4] The complete statement regarding the constituents of portland cement will be found in "Properties of the calcium silicates and calcium aluminates occurring in normal portland cement," by Bates and Klein. *Technologic Paper* 78, Bureau of Standards, Washington (1917). Two thorough articles on this study are: E. S. Shepherd and G. A. Rankin, *Ind. Eng. Chem.*, 3, 211 (1911), and G. A. Rankin, *ibid.*, 7, 466 (1915).

4 to 8 gallons of water are used per sack of cement; not more than 2½ gallons will chemically combine with each sack of cement, to become part of the structure. The rest evaporates. Too rapid evaporation is undesirable; it is retarded by keeping the surface covered with straw, and by wetting it (curing). The purpose of curing is to prevent evaporation until after hydration has proceeded well along to completion.

The setting of pure portland cement is so rapid that, if it were uncontrolled, the cement would be useless; the addition of small percentages of calcium sulfate (as gypsum) gives the desired retardation. The initial set of pure cement occurs in 6 minutes; 3 per cent of gypsum lengthens the period to 3 hours.

In the manufacture of portland cement the proportions of lime (generally as limestone), alumina, and silica (as clay or shale) are carefully adjusted for example, 77 per cent limestone, 23 per cent shale, and the mixture is sintered; in natural cements a suitable rock is generally used without admixture, so that the composition is variable, and there is no sintering. Considerable amounts of portland cement are made from the iron blast-furnace slag.

Portland cement sets under fresh water as well as in air, it is therefore also a "hydraulic" cement; for sea water, its iron content should be raised to several parts per hundred.

Raw Materials. Limestone and clay are the necessary raw materials; pure limestone is not usually chosen, except for adjusting the final mixture; rather argillaceous limestones, which are more common and which can neither be used for making quicklime, nor in a blast furnace, are used. The "cement rock" is such a limestone, which contains the necessary constituents in proportions so nearly right that only slight adjustments are necessary. The plant is erected as near to the deposit as possible; the rock is hauled perhaps 1000 to 2000 feet in the most favorable cases.[5] The material is blasted in the quarry,[6] and brought to gyratory crushers,[7] which reduce the rock to egg size. The addition of correcting amounts of limestone, for example, takes place at this stage. The properly mixed materials are generally dried in a short (40-foot) rotary furnace with inside heating, then crushed further in a swing-hammer mill,[7] sieved, and finally pulverized in a Raymond suction mill,[7] or similar pulverizer. The material ready for the furnace is of such fineness that 90 per cent will pass through a 100-mesh sieve. The relative proportions of raw materials must be such that the analysis of the final cement falls between the following limits:

		Limits (Per cent)	Average (Per cent)
Lime	CaO	58–65	61.5
Silica	SiO_2	20–25	22.5
Alumina	Al_2O_3	4–11	7.5
Magnesia	MgO	0–4	2.0
Iron	Fe_2O_3	0–4	2.0
Sulfur trioxide	SO_3	0–1.75	1.0
Alkali	Na_2O, K_2O	0–3	1.5

[5] Examples: Bath, Nazareth, Martin's Creek, near Easton, Pa., and Alpha, just across the river in New Jersey.

[6] Which may be a hill, such as at Martin's Creek.

[7] Chapter 44.

Instead of limestone, marl, a deposit of a geologically more recent origin, may be used; in such a case, it is often conveyed, wet, through pipes to the plant, and ground wet; the clay is then also ground wet. In one large plant with wet mix, the raw materials are ground in 8-foot diameter by 30-feet long, 3-compartment Compeb mills, turning at the rate of 19 r.p.m; 93 per cent must pass through 200 mesh. In four plants, oyster shells and clay are the raw materials. After mixing and settling, the slurry may be fed directly into the kiln, to be dried by the outgoing gases. In plants using a wet mix, the furnace must be longer. Of the 141 plants in the United States, 81 ground wet, while 60 operated dry, in 1945. Limestone and clay is the most frequent combination, roughly 3 parts of limestone to 1 of clay.

During the furnacing carbon dioxide and water of constitution are lost, so that there is a shrinkage in the material obtained; it is usually estimated that 1.7 tons of raw materials produce 1 ton of cement.

The slag from the iron blast furnace may be so adjusted that it is well suited for the manufacture of portland cement; it is mixed with limestone, with perhaps another addition to reach the desired percentages, and furnaced as the rock mixtures are. The shrinkage in this case is somewhat less.

By means of froth flotation the raw materials which may be purified from micas, talc and sulfides which form the concentrate, are discarded, while the calcite, quartz and composite rock particles are the tailings. The flotation agents are aliphatic amines, in quantities much below 0.4 pound per ton of feed.

TABLE 26.—*Percentage of total production of portland cement in the United States according to raw materials.**

	1935	1942	1945
Cement rock and pure limestone	31.0	27.0	19.8
Limestone and clay or shale	58.8	63.4	71.4
Marl and clay	1.9	1.7	2.0
Blast furnace slag and limestone	8.3	7.9	6.8

* "Minerals Yearbook," 1945.

The Portland Cement Rotary Furnace. The furnace generally used in the United States is a brick-lined steel cylinder, slightly inclined from the horizontal; it is mounted on idling wheels of small diameter, and carries a gear wheel meshing with a pinion wheel which rotates the cylinder at the rate of one-half to two r.p.m., according to size. The operation is continuous; raw material is fed in at the upper, colder end, and the clinker is discharged at the lower, hot end. The flame is formed by pulverized coal, atomized oil, natural gas, and sometimes producer gas, at a burner placed in the stationary hood into which the lower end of the cylinder fits. The hood acts also as receiving box for the discharged material, called the clinkers. An extension of the stationary box reaches into a smaller cylinder inclined from the horizontal in the opposite direction, and also rotated; as a result, the clinkers, after reaching the smaller cylinder through the chute, move forward toward the discharge opening. A current of air sweeps over the clinkers and enters the burner hood, there to become the air of

combustion for the fuel; by preheating the air in this way, the temperature reached in the hotter end of the furnace is raised, while the clinkers are cooled.

The size of the kiln has been gradually increased.[8] The kilns studied and used as models in this account are 11 feet in diameter and 250 feet long. The kiln is inclined ¾-inch to the foot, toward the hot end, which is also the clinker discharge end. The feed, in this instance a slurry feed, enters at the colder and upper end. There is a lining of bricks at the hot end which is 9 inches thick for 100 feet; then a lining 7 inches thick for 110 feet; over the last 40 feet the shell is bare, except for lifters. The kiln is rotated by a girth gear at the rate of 0.6 r. p. m. The direction of rotation is counter-clockwise, as one faces the discharge end. The rated maximum capacity for

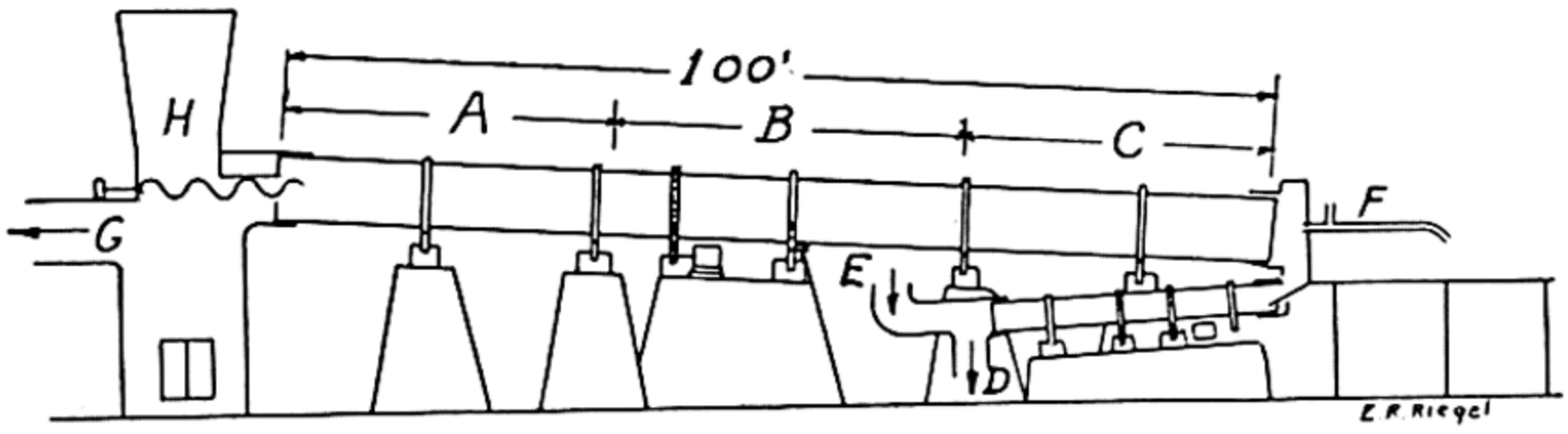


FIGURE 60.—The rotary portland cement furnace; *F*, pulverized coal burner; *H*, feed bin with conveyor; *D*, discharge of clinkers; *G*, passage for fire gases to boilers and stack; for zones *A*, *B*, and *C*, *see* text.

each kiln is 2100 barrels a day (at 376 lbs. each); the usual rate is nearer 1500. The output is varied by varying the amount of feed. The clinker is delivered to a tubular cooler similar to the kiln, but only 90 feet long and 9 feet in diameter. The fuel is powdered coal, here 88 pounds to the barrel of cement, which is considered a good performance; 100 and 120 pounds[9] is not uncommon. A mill near Montreal is said to burn only 60 pounds of coal to the barrel. The secondary air is preheated in the cooler; the flame is 20 and even 35 feet long. The temperature in zone A (Fig. 60) is moderate; here the moisture is driven out and the materials heated. In zone B, the middle zone, the temperature averages 1800° F. (982.2° C.); the carbon dioxide is expelled from the limestone. In zone C, the maximum temperature of 2800° F. (1538° C.), which may be increased to 2900° F. (1593° C.) or dropped below if desired, is developed. The clinker is discharged at the hot end in a stationary hood with discharge piece leading into the cooler. The gases pass from the feed end to an electrical precipitator and thence, with temperature between 900 and 1100° F., through a 15-ft. diameter stack 235 feet high to the atmosphere. In the wet process, the time required for a pound of slurry to travel through the kiln varies from two and a half to six

[8] In 1935, there were 193 kilns 125 feet long, 176 between 150 and 199, and 94 between 200 and 260; 9 were between 261-299, 8 between 300 and 350, and 8 between 372 and 400 feet in length, the maximum was 400. 35 were as short as 40 to 60 feet. "Fuel efficiency in cement manufacture, 1909-1935," WPA and Bureau of Mines, report E-5, April 1938.

[9] "Cements, Limes, and Plaster," by E. C. Eckel, New York, John Wiley and Sons, Inc., 1928.

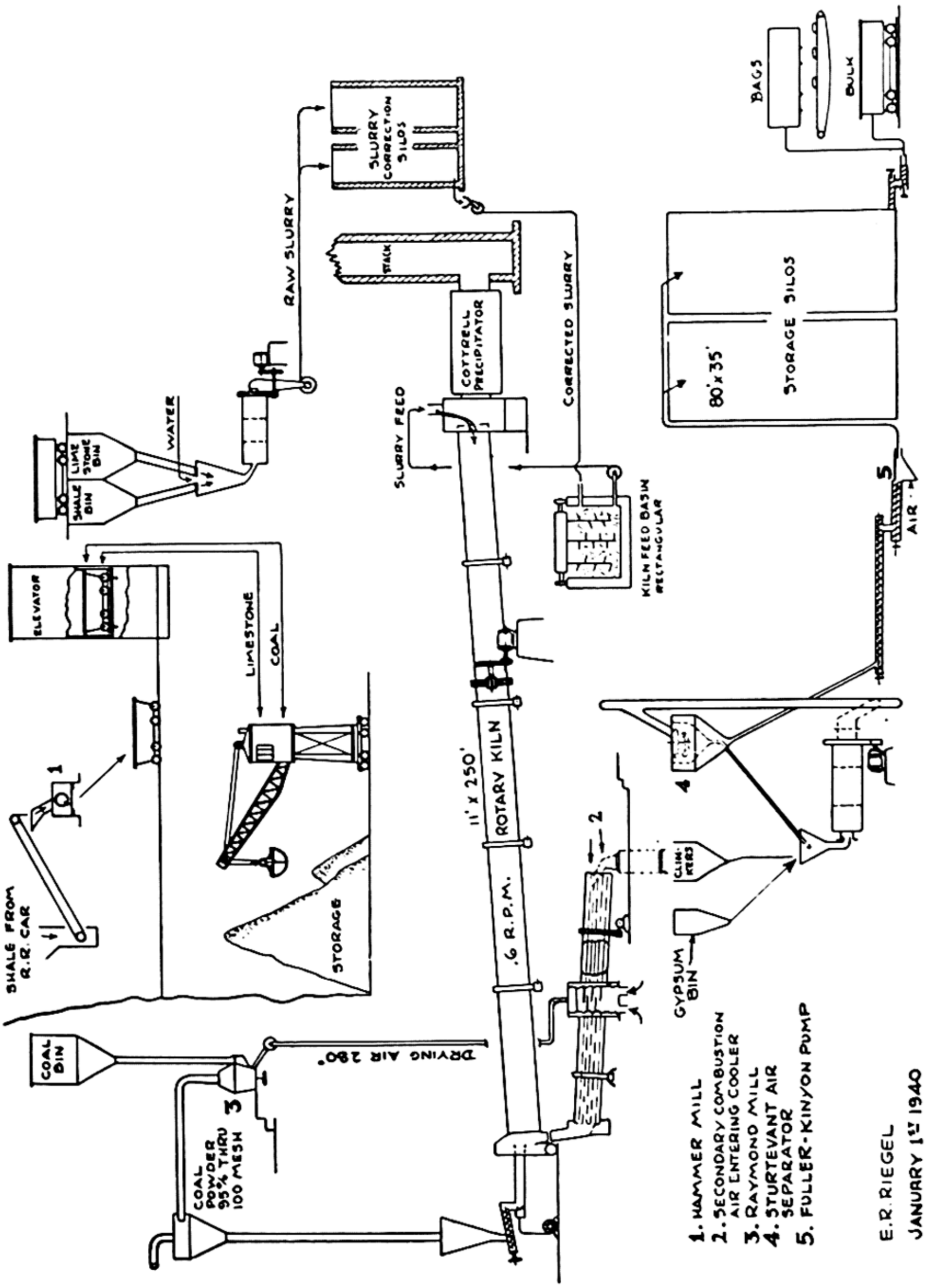


FIGURE 61.—Pictorial flow sheet for a portland cement plant with wet mix.

hours, depending upon the length of the kiln. In the shorter dry process kilns a pound of charge requires only from three-quarters to two hours to pass through.

The average fuel consumed per barrel of cement produced was as follows (1945): coal, 127.2 pounds; oil 0.205 barrel of 42 gallons; natural gas, 1,420 M cubic feet. Of the several kinds of fuel, coal formed 53.3 per cent of the total, oil 9.5, natural gas 9.2, and mixed fuels the balance.

In Europe the Lepol kiln has been developed;[10] it operates with a fuel consumption of 45.6 pounds of coal per barrel of clinkers. In 1932, there were 34 Lepol kilns in Europe, one at San Sebastian in Spain. In the United States one Lepol kiln was reported installed and operating successfully in Spokane, Wash.

The volume of the charge is such that over the greater length of the kiln it forms a stream about 18 inches thick. At the burning zone, it seems much higher. A sort of nose is built up by the moving charge, and it seems that it must crash forward toward the hot end, yet it does not. In the last few feet of the kiln, this stream is about 6 inches. In the hot zone there is no melting to form a fluid, but merely a softening to a dough-like mass, in which there is nevertheless a liquid phase, which is estimated to make up 25 per cent of the whole. The clinker produced is homogeneous, consisting of a hard mass with numerous gas pockets; from the kiln studied, the clinker is quite uniformly $\frac{3}{8}$-inch in diameter, and black. It is considered good practice today to form the hottest zone as close to the discharge as possible. The hot spot, for example, may be 35 feet and, the highest temperature 12 feet from the clinker discharge end; the result is a rapid chilling of the clinker as it is discharged, so that the magnesia in the liquid phase does not have time to form the crystal, periclase; instead, all the liquid phase becomes a harmless, and in some ways a beneficial glass. Periclase is avoided because it is the main cause for "delayed expansion," a property tested for by the autoclave test. Normal cement may have a "delayed expansion" of 0.5 per cent; special cements 0.02 to 0.04 per cent.

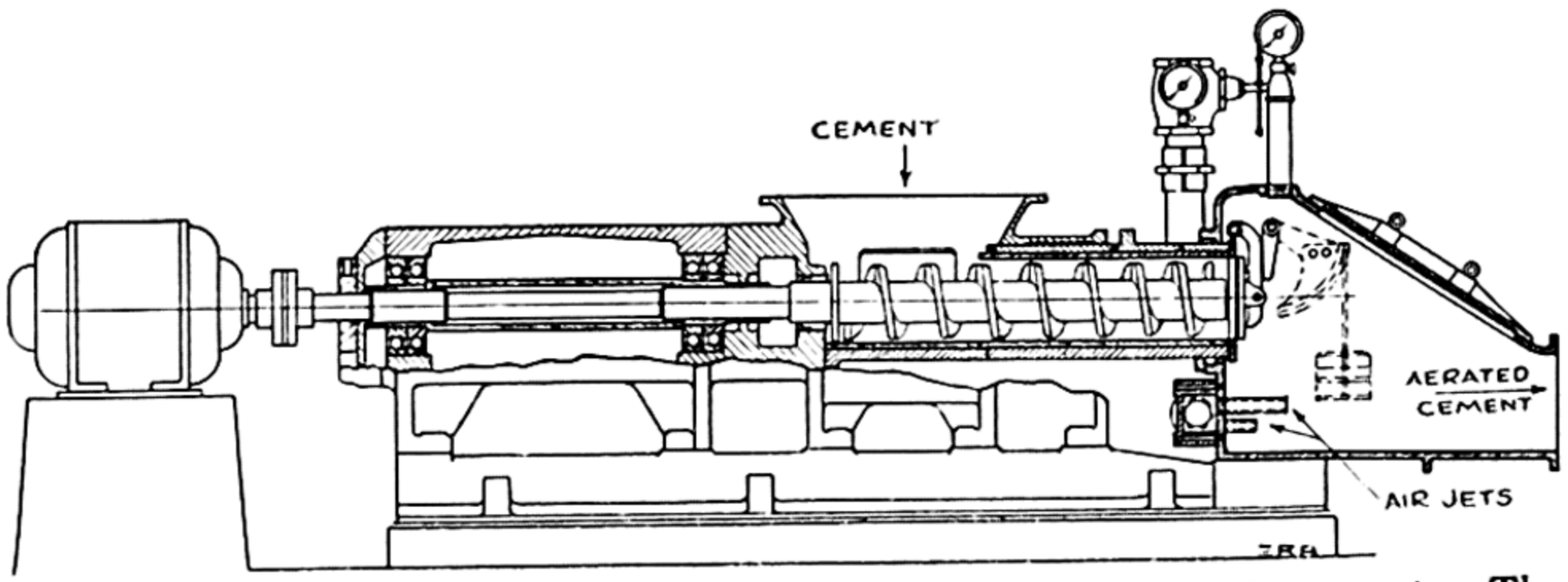


FIGURE 62.—The Fuller-Kinyon pump for conveying portland cement. The screw feeds the cement powder into aeration chamber, where the air jets deliver a stream of compressed air which unites with the powder to form a fluid mass which travels 600 feet laterally and then 95 feet vertically to the top of storage silos.

[10] Report by the inspection committee, "New cement burning process," *Rock Products*, 35, 42-47, 1932.

The clinker is ground in various ways; one of the more modern devices is a three-compartment Compeb ball mill; the product goes to an air separator which returns the tailings for further grinding. It is at the grinding mill that the retarder, gypsum, is added. Cement is moved by a Fuller-Kinyon pump, a Robinson air-activated conveyor, or other means, to storage silos, and thence to a bagging machine, or to bulk loading. In this particular plant, it takes 592 pounds of raw materials to make a barrel of cement of 376 pounds; hence the shrinkage is 36.5 per cent.

The fineness of the powdered cement is a matter of importance. It is still customary and useful to speak in terms of mesh fineness, as for example, portland cement tests 98 to 99 per cent through a 200-mesh sieve, and 90 per cent through a 325-mesh sieve. However, the fineness may also be expressed in terms of "specific surface," that is, the surface in square centimeters of one gram of cement.[11] The test is performed by dispersing 0.3 gram of the powder in 15 cubic centimeters of kerosine; 6 drops of oleic acid are added, and the whole is then dispersed further in 335 cubic centimeters of kerosine. The turbidity is measured at various levels by means of the light transmitted, as recorded by a photoelectric cell. For normal portland cement, the New York state requirement is 1750 specific surface. The Federal requirement is 1500.

TABLE 27.—*Approximate size distribution of an average portland cement with the rate of hydration.**

Size in microns	Percentage of total	Color	Time required for complete hydration
Under 10	21	pure white	less than 24 hours
10–20	16	white	24–48 hours
20–30	8	nearly white	4 days
30–43	30	very light brown	7 days
44–70	16	brownish gray	28 days or more
Over 74	9	gray	indefinite

200-mesh is equivalent to 74 microns, 325-mesh to 43 microns.

* *Concrete*, **38**, No. 4, p. 16 (1931).

Portland cement meets specifications and additional tests which have become official.[12] The neat (unmixed) cement must have a tensile strength of 500 lbs. per square inch after 7 days; the cement mixed with 3 parts of sand must have a strength of 200 lbs. after the same period.

The strength of concrete, which is composed of cement 1000 lbs., sand 1500 lbs., and crushed stone 3000 lbs., is greatly increased by imbedding in it twisted square steel bars, or wire netting similar to stout fencing; it is then called reinforced concrete.

There are available precast reinforced concrete joists and slabs which simplify roof construction (Lith-I-Bar).

Magnesium fluosilicate,[13] $MgSiF_6 \cdot H_2O$, in solution is applied to the

[11] Federal specification SS-C-158, September 30, 1936; and SS-C-191a, same date.

[12] "Standard specifications and tests for portland cement; adopted by the American Society for testing materials, and by the U. S. Government," 1917, 47 p., obtainable (10 cents) from the Superintendent of Documents, Washington, D. C. Bur. Foreign and Domestic Commerce, Industrial Standards, No. 1.

[13] Chapter 2. For informative leaflets on magnesium fluosilicate send request to General Chemical Division, 40 Rector St., N. Y., or to L. Sonneborn Sons, Inc., 88 Lexington Avenue, N. Y.

surface of cement roads and walls to protect them from weathering; such protection is not absolutely necessary, for the cement structure is permanent without it; but the surface becomes smoother and the weather-resistance properties are increased. Pipes for sewers, as large as 5 feet in diameter, are made of concrete, and are harder and stronger if treated with magnesium fluosilicate solution.

The recovery of potash from cement furnace gases is discussed briefly in Chapter 8.

The high early strength of portland cement, a property possessed by the normal cement, may be increased by finer grinding or by raising the calcium oxide content to obtain a high ratio of tricalcic silicate to dicalcic silicate (such as 7 or 8 to 1, instead of the normal 5 to 4). In the manufacture of *high early-strength portland cement* either of these two methods or both may be employed to obtain the desired result. The sieve test may be 99.5 per cent through 325-mesh; the specific surface must be not less than 1900.[14]

Other *special cements* are listed below. The aluminous cement resists the action of sulfate-bearing waters.[15]

TABLE 28.—*Composition of normal and modified portland cement*
(In percentages)

	Normal	High early-strength	Low heat	Aluminous
CaO	64	65	60	40
SiO_2	23	20	23	5
Al_2O_3	6	6	5	40
Fe_2O_3	3	3	5	15
MgO	2	1.5	2	.1
SO_3	2	2.5	2	.1

The production of portland cement fluctuates considerably. It is now rising from a low in 1944, when it totalled 92,152,399 barrels for all types. The production in 1946 was 163,805,000 barrels, and the estimate for 1947 is approximately 185,000,000 barrels.

TABLE 29.—*Production figures for normal and special portland cements (1945).**

	(barrels, 376 lbs each)
General use and moderate heat types	94,998,226
Special types: High early strength	5,487,460
Low heat	35,715
Sulfate resisting	5,141
Oil well	1,231,756
White	425,299
Portland-puzzolan	212,156
Total, including miscellaneous	104,288,647

* "Minerals Yearbook," 1946.

The average price received at the mill was $1.63 per barrel (1945).

LIME

Lime is the oxide of calcium, CaO, and is obtained by calcining limestone. The reaction $CaCO_3 \rightleftarrows CaO + CO_2$ is reversible, but it may be run com-

[14] Federal specification SS-C-201.
[15] *Ind. Eng. Chem.*, 18, 554 (1926).

pletely to the right by removing the carbon dioxide from the system; this is done in the kiln by the fire gases on their way out. Limestone is calcined in two main types of kilns, the vertical or shaft kiln, and the horizontal, rotary kiln.

The shaft kiln is illustrated in Figs. 63 and 64; limestone is fed in at the top, the fire gases enter at a short distance from the bottom, and the finished lime is drawn out at intervals, or continuously, at the bottom. The temperature may be 1000° C. (1832° F.) in the kiln proper; it will be lower at the exit, because the gases preheat the entering charge. The carbon

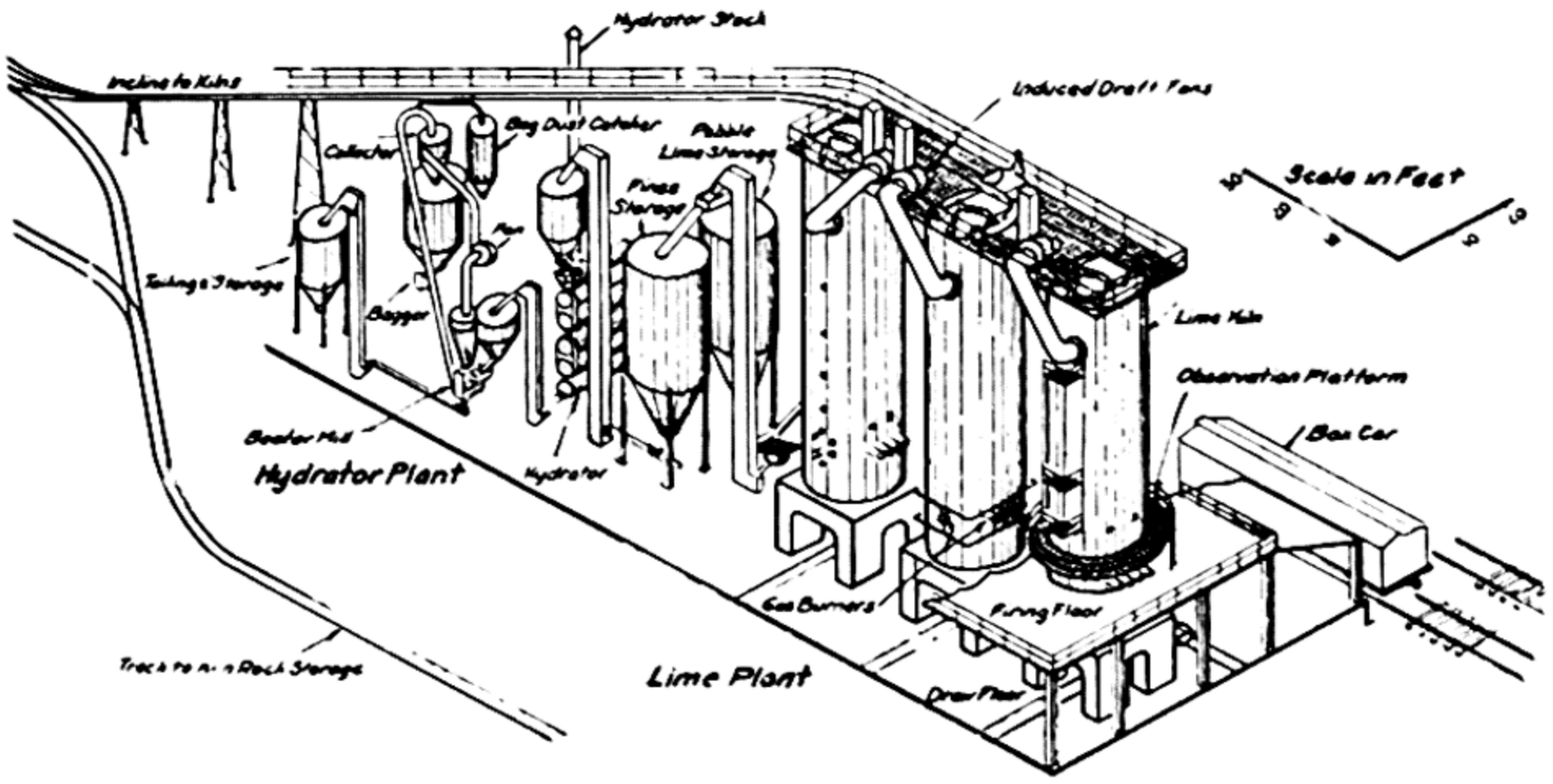


FIGURE 63.—Isometric drawing of three gas-fired lime kilns with sealed tops. The induced draft fans return exhaust gas, to temper and lengthen the gas flame. The exhaust gas leaves the kiln at a temperature between 700 and 800° F. The kilns are about 60 feet high. Hydrator plant is shown. (*Rock Products*, p. 86, January 15, 1935; plant designed by Mr. Victor J. Azbe.)

dioxide passing out may be recovered; it may be returned, at least in part, to the burners in order to temper and lengthen the flame, and the balance wasted. Too high a temperature is avoided because it tends to harden the lime by fusion of impurities. The maximum capacity of a shaft kiln is reckoned generally as one ton per square foot of shaft area per day, so that a kiln with shaft 9 feet by 7 feet, with about 60 square feet area, will produce 50 to 60 tons of high-grade lime per day. The shaft kiln is a heat exchanger as well as a reactor; the solids traveling down take heat from the gases which are rising; the operation illustrates the counter-current principle. The fuel[16] may be natural gas, producer gas, oil, wood, or coal; in the latter case, the modern construction places the coal in outside fireplaces, admitting only the fire gases. The lime leaving the kiln is crushed to the size required, and screened.

Lime may also be calcined in a rotary kiln similar to the cement kiln but generally smaller, consisting of a steel shell lined with refractory bricks, set near the horizontal. The fuel may be those enumerated for the shaft kiln, with the addition of the increasingly favored pulverized coal. A rotary

[16] "Burning lime in a gas-fired continuous kiln," by W. D. Mount, *Chem. Met. Eng.*, 20, 428 (1919).

kiln handling pebble lime may be 135 feet long, 8 feet in diameter, making 1 revolution in 95 seconds; the pebbles are discharged at red heat, 1660° F. (904.4° C.) while the furnace itself may have a temperature of 2500° F. (1371° C.). A drag conveyor and a bucket elevator bring the hot pebbles to a rotary cooler, from which they pass to the shipping containers. It is interesting to note that the general shape and size of the pebble is preserved, so that grading of the calcite pebble may be done in Michigan, for example, the pebbles transported to the site of the kiln (Buffalo), and there calcined, without further grading. The kiln described furnishes 72 tons of lime

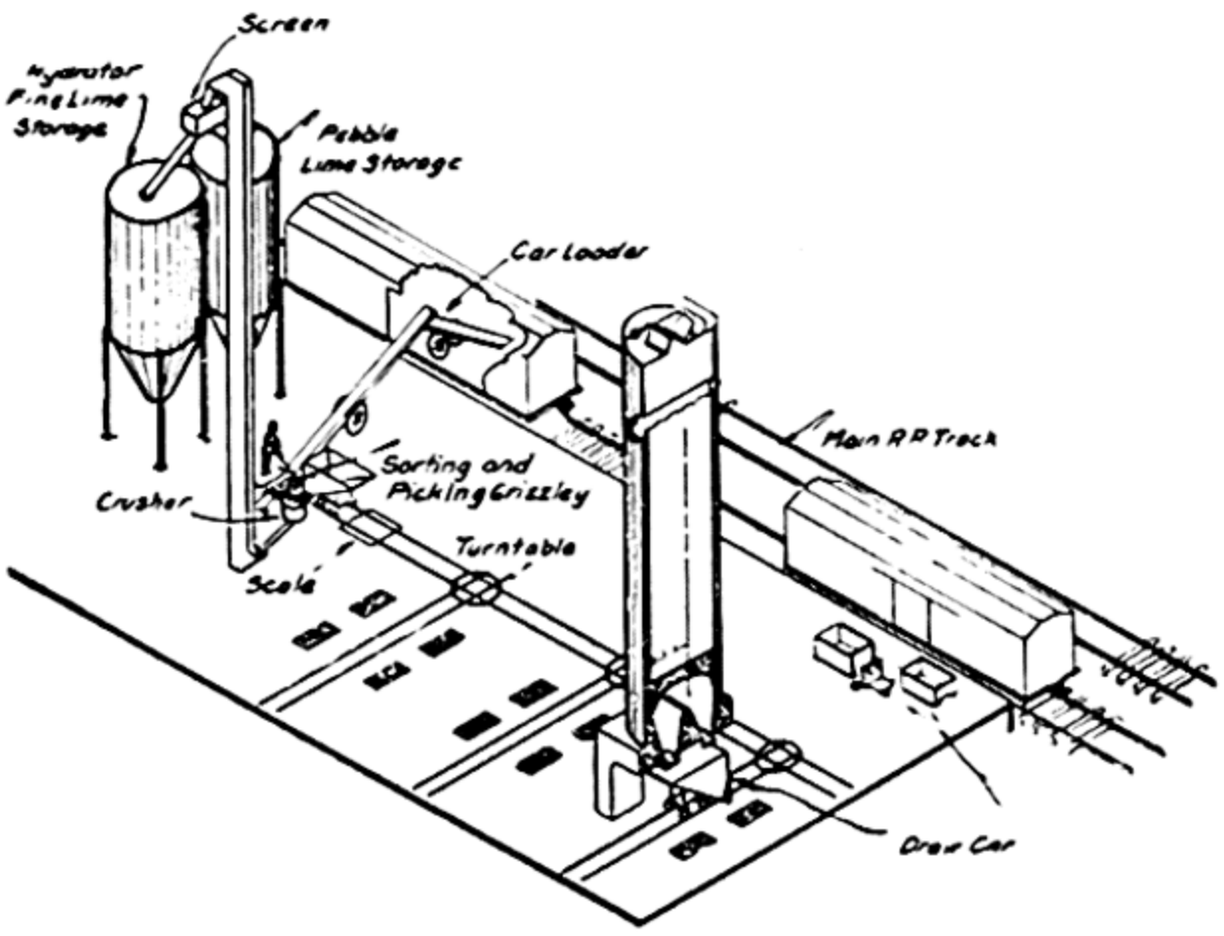


FIGURE 64.—Plan of lime handling system with kiln cut away to show inner construction.

per day, operating continuously; one ton of coal is burned for 2½ tons of lime produced—a greater consumption than that in the shaft kiln. In the latter, 12 per cent coal on the weight of the product is very good practice; the theoretical consumption is 11.2 per cent. It will be evident that for efficient fuel utilization, the shaft kiln leads.

TABLE 30.—*Analysis of limestone and the lime produced from it in a rotary kiln.*

	Stone taken from feeder at No. 1 kiln	Pebble lime from discharge end of cooler
Loss on ignition	43.68	0.22
SiO_2	.56	1.02
R_2O_3	.48	.68
CaO	54.66	97.04
MgO	.51	1.10
Sulfur	.138	...
SO_3	....	.03
$CaCO_3$	97.55	...
$MgCO_3$	1.07	...
Available CaO	....	94.76
30-mesh residue	....	.24

Not infrequently the same company will have both shaft and rotary kilns, the shaft kiln for large stones, the rotary for fines.

A new type of calcining unit was installed in a lime plant at Provo, Utah, in 1945. It is an inclined stationary furnace with a slope of 35°. It is reported to be very economical of fuel.

A pebble of lime, when treated with a limited amount of water, develops heat, swells, and soon disintegrates into a fine powder consisting of hydrated lime:

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

TABLE 31.—*Lime sold by producers (189) in the U. S. in short tons, and price per ton.**

	1940		1945	
Quicklime	3,501,104	$6.69	4,565,551	$7.56
Hydrated lime	1,385,825	7.59	1,355,028	8.43
Total	4,886,929	6.95	5,920,579	7.76

* "Minerals Yearbook."

Much of the lime produced is changed into hydrated lime, for agricultural purposes and others. Lime serves for many purposes; it is as useful as an alkali as sulfuric acid is as an acid in the chemical industries. It is used in mortar, plaster, insecticides, refractory bricks, in metallurgy, in the paper industry, for water treatment, and for hundreds of other purposes.[17]

TABLE 32.—*Consumption of lime in the several kinds of uses in the U. S., (totals for the two kinds of lime).**

	1940		1945	
Agricultural	364,823		373,410	$7.78
Building	1,010,435	$5.71	549,547	8.93
Chemical industries	2,643,762	6.20	3,810,288	7.21
Refractory (dead-burned dolomite)	867,909	7.98	1,187,334	8.94

* "Minerals Yearbook."

GYPSUM PLASTER

Gypsum plaster is made by removing most of the water of crystallization from gypsum, $CaSO_4 \cdot 2H_2O$, by gentle heat; the plaster so produced, when mixed with water, may be spread and shaped, and in a few hours it sets to a hard mass. Gypsum plaster is almost universally used for coating the inner walls of dwellings. It is often called plaster of paris, because huge deposits of gypsum are found in Paris and in its neighborhood, and these were the first to be worked.[18]

While limestone is found exposed or covered by an overburden easily stripped off, permitting open pit operations, gypsum generally occurs at greater depths and shaft operations are the rule. It may be said also that limestone is far more common than workable gypsum deposits. This is partly because only rock with the composition $CaSO_4 \cdot 2H_2O$ may be used; if it contains less water, calcining it does not produce a material which sets with water. A seam 3 feet in thickness is considered valuable, if it has a reasonable extent; the deposits near Buffalo have this thickness and have an area of roughly 1 square mile.[19] The depth at which they lie averages 80 feet. The method of mining is by entries, and "rooms," 250 feet deep and

[17] See I. C. 6884R, "Lime," by Oliver Bowles and D. M. Banks, revised by Duncan McConnell, Bureau of Mines, October, 1941.

[18] It was the study of gypsum plasters which led the French chemist, Le Chatelier, to his investigation of the constitution of portland cement.

[19] Akron, Scottsville, Oakfield, and Clarence, New York.

25 feet wide.[20] Holes are drilled by electric augers; 20 per cent dynamite is used for blasting, and is exploded by a fuse. The broken rock is loaded into the mine cars which are pulled by an electric (D. C.) locomotive to the shaft or incline. Gypsum rock is nearly white, and has large crystals; it is a soft rock. Gypsum mines do not require artificial ventilation.

Gypsum is obtained from 52 active mines (U. S.), situated in California, Iowa, Michigan, Nevada, New York, Texas, and elsewhere. In 1946, Michigan led with 1,120,070 short tons (4 mines), while New York was second with 814,999 tons (7 mines).

The mine cars are dumped into a gyratory crusher [21] with a pot 11 feet deep; the product is elevated to a rotary screen, which separates the fines from the lumps, which are about egg size. The fines are shipped to portland cement plants.[22] The lumps are fed to a rotary drier, a horizontal steel cylinder 30 feet long, with internal firing; the rock is passed through so fast that it attains a temperature of only 150° F. (65° C.). The dried rock is more easily crushed further and pulverized; the devices used are a swing-hammer mill [21] followed by inclined flat screens; the material which passes through the screen is sent to a Raymond suction mill;[21] the tailings (on the screen) are returned to the swing-hammer mill. The pulverized material from the Raymond mill is sent to the calciners, upright cylindrical vessels with slow-moving agitators, and several horizontal flues through which fire gases pass. The fine powder remains in the calciner 1 hour; the temperature is about 350° F. (177° C.); no more than three-quarters of the water of crystallization is removed. After calcining, the powder is white; it is discharged through a door at the base of the calciner which leads to conveyors; these bring the material to the storage house.

Calcined gypsum is made into wall plaster by the addition of asbestos, hair, shavings, sweepings from packing houses, and dextrin, according to specifications. Without addition, it is plaster of paris. Considerable amounts are used at the mill itself to make plaster boards,[23] which may then be placed on the walls of dwellings with little labor, and by any one unskilled in plastering. The manufacture of these plaster boards is largely automatic. The calcined rock is mixed with 8 per cent (by weight) of selected sawdust on a conveyor which passes into a shallow tank where it takes up the right amount of water for setting. The wet mass is dumped on a sheet of paper, leveled, and covered by a second sheet; the edges are folded over, and the sheet pulled continuously toward the knife. By the time it reaches the latter, 12 minutes have elapsed. An accelerator added to the original mix hastens the hardening, so that the board may be handled, although it is not dry. The knife cuts it into appropriate lengths, which are dried in tunnels by a stream of warm air.

Low density and therefore light-weight gypsum plaster boards and products are obtained by mixing a dilute hydrogen peroxide solution with the plaster of paris; the gas slowly developed (O_2) remains in the mass.

[20] *Compare* coal mining in Chapter 12.
[21] Chapter 44.
[22] *See* the first part of this chapter.
[23] Examples: "Best Wall," "Sheet Rock."

The production of all building materials, including gypsum products, was stimulated by the Veterans Emergency Housing Act, of May 22, 1946, as will be seen from Table 33.

TABLE 33.—*Gypsum products sold or used in the United States.**

	1945		1946	
Uncalcined (short tons)				
Portland cement retarder	664,247	$ 2.26	1,135,853	$ 2.60
Agricultural gypsum	462,217	3.71	471,902	3.93
Building plasters				
Base-coat (short tons)	640,276	9.53	1,507,115	10.68
Total cementitious	879,538		1,938,223	
Prefabricated				
Lath (short tons)	445,497	13,64†	865,682	16.17†
Wallboard	1,023,537	22.53†	1,517,035	22.99†
Tile	104,943	42.62†	108,721	47.92†
Total prefabricated	1,801,891		2,593,948	

* "Minerals Yearbook."
† Value for 1000 sq. ft.

Gypsum plaster is valuable for making casts; on setting, there is an increase in volume of 1 per cent and as a result, the casts are sharp. For temporary buildings imitating famous examples of architecture, such as for the International Exposition in Paris (1937), gypsum plaster is used in vast quantities.

An artificial gypsum has been mentioned in Chapter 7.

MAGNESIUM OXYCHLORIDE CEMENTS

This name is given to cements made by adding a strong solution of magnesium chloride to magnesium oxide, usually called calcined magnesia. A filler such as small stones, wood flour, or cork, is mixed into the paste. After a short time the paste sets to a hard mass approximating portland cement in strength. The proportions of solution and magnesium oxide must be properly chosen and strictly observed. The cement, after setting, takes a high polish; it is used only for interior work such as floors in hospitals and public buildings. Sorel cement is a magnesium oxychloride cement.

OTHER PATENTS

U. S. Patent 2,069,164, rotary kiln; 2,217,685, flotation concentration for calcite.

PROBLEMS

1. Since three-quarters of the water of crystallization of the gypsum is removed during calcination, show that the finished material retains 6.2 per cent water.
2. A lime kiln delivers 27 tons of lime per day; how much limestone must be fed in, assuming both substances to be pure and the burning perfect?
3. The amount of fuel per barrel of finished Portland cement is given in the text (an average). For a furnace producing 215 tons of cement per day, how many tons of coal must be provided?
4. A Portland cement contains its calcium silicates in the proportions of 5 tricalcium silicate molecules to 4 dicalcium silicate. Compute the absolute amount on the basis of 23.46 per cent SiO_2 in the Portland cement. How much lime (CaO) must be added to change the ratio of the calcium silicates to the new one, namely 8 molecules of tricalcium silicates to 1 of dicalcium silicate? How much limestone is

required, if it contains 95 per cent $CaCO_3$? All the lime added will react with dicalcium silicate. What is the limestone quantity to be added in terms of the original Portland cement?

Reading References

"Cements, limes, and plasters," E. C. Eckel, New York, John Wiley and Sons, Inc., 1928.

"Cement," Bertram Blount, London and New York, Longmans, Green and Co., Ltd., 1920.

"Le Plâtre," Pierre Jolibois, *Bull. soc. chim.* (4), 41, 117-135 (1926).

"The Portland cement industry," Richard K. Meade, *Ind. Eng. Chem.*, 18, 910 (1926).

Lime symposium, *Ind. Eng. Chem.*, 19, 550-605 (1927).

"Calcium sulfate retarders for portland cement clinkers," Ernest E. Berger, *Bur. Mines Tech. Paper* No. 451 (1929).

"Rotary kilns vs. shaft kilns for lime burning," Richard K. Meade, *Ind. Eng. Chem.*, 19, 597 (1927).

"The rate of calcination of limestone," C. C. Furnas, *Ind. Eng. Chem.*, 23, 534 (1931).

"The action of sulphates on the components of portland cement," T. Thorvaldson, V. A. Vigfusson and R. K. Larmour, *Trans. Royal Soc. Canada*, 31, section III, 295 (1927).

"Multistage process for burning portland cement clinker," Robert D. Pike, *Ind. Eng. Chem.*, 22, 148 (1930).

"Modern developments in the chemistry of portland cement," F. M. Lea, *J. Soc. Chem. Ind.*, 53, 639 (1934).

"Liberation of heat during the hydration of concrete," N. Davey, *J. Soc. Chem. Ind.*, 53, 343T (1934).

"The rate of hydration of portland cement and its relation to the rate of development of strength," F. M. Lea and F. E. Jones, *J. Soc. Chem. Ind.*, 54, 63T (1935).

"Flotation as applied to modern cement manufacture," C. K. Engelhart, *Ind. Eng. Chem.*, 32, 645 (1940).

"A new dry-process cement plant in Argentina," V. K. Newcomer, *Pit and Quarry*, 32, p. 36, with a plan on p. 38, and a flowsheet on p. 43 (1939).

"Universal Atlas plant at Leeds, Ala., firm's only wet-process operation," W. E. Trauffer, *Pit and Quarry*, 32, p. 32, with a layout on p. 34 (1939). (Universal Atlas now has a second wet process plant, at Northampton, Pa.).

"The chemistry of portland cement," Robert Herman Bogue, New York, Reinhold Publishing Corporation, 1947.

"Calcination of dolomite in large shaft kilns," C. C. Brumbaugh, *Chem. Eng. Progress*, 44, 881 (1949).

The great importance of ceramics to the chemical industries is evident when it is pointed out that the steel shells of portland cement furnaces, of Bessemer steel converters, of sulfite pulp digesters, of gas producers and water-gas generators are lined with bricks; in addition, fire boxes under boilers, reverberatory furnaces for varied purposes, and tank furnaces for glass depend for their proper construction upon ceramics. These are only a few examples and leave out of reckoning building bricks and stoneware.

Chapter 10

Ceramic Industries*

Ceramics is the art of producing useful articles entirely or chiefly from raw materials of an earthy nature by high-temperature treatment during manufacture. The principal raw material is clay, which may be used alone or with the addition of other substances. Some of the more important products of the industry are: building brick and tile, sewer pipe and electrical conduit, drain tile, refractory bricks of all kinds, electrical and chemical porcelain and stoneware, whiteware such as sanitary ware, art ware, dinnerware, china, floor and wall tile, porcelain enamels and abrasives.

The clays used differ widely in their properties and are so selected and combined with one another as well as with other raw materials as to give a composition having the best working properties in manufacture, consistent with the desired properties of the finished ware. The principal property of clay is its plasticity, which permits objects to be formed and molded from it by various methods. This property in turn depends on the colloidal content of the clay, the state of hydration, the fineness of the particles, the amount and kind of soluble salts present and to some extent the amount of organic matter present. Highly plastic clays are known in the industry as "fat" clays; those of lower plasticity are called "lean" clays. The plasticity of clay may be considered the resultant of two properties: deformability, which allows shaping, and tenacity, which resists tearing.

In drying and firing an all-clay body, considerable shrinkage occurs which tends to crack and warp the molded piece, making it useless. The shrinkage is more pronounced with clays of high plasticity, less so with clays of medium plasticity, and least with clays of low plasticity. The shrinkage is reduced by the addition of non-plastic and thus non-shrinking materials. One of these is calcined clay, for clay loses its plasticity and shrinkage in the same measure as its water of hydration is removed during the calcination. Other non-plastics used for this purpose are ground flint (SiO_2), highly fired clay known as grog, calcined kyanite, and many other ground or crushed minerals. In general the strength and hardness of a ceramic body before and after drying and firing depends on the amount and plasticity of the clay used. The lower these are, the weaker the article; the greater they are, the harder and stronger the article, and the greater the shrinkage of the piece.

* In collaboration with Mr. William Horak, Manager, Refractory Department, Hartford-Empire Co., Hartford, Conn.

Another property of clays of great importance is their fusion point, which differs according to their impurities, geological history, and substances purposely admixed. The fusion point of clays decreases in general with increase in silica over the theoretical composition of pure clay ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and increases with increase in the alumina content. Naturally occurring impurities, such as iron oxide, titanium oxide, alkali oxides, and alkaline-earth oxides, also lower the fusion point. The fusion point of ceramic compositions is in fact controlled by the addition of ground minerals which contain such oxides, as for example feldspar, which is widely used for this purpose. Others are whiting ($CaCO_3$), barium oxide, strontium oxide, beryl, and beryllium oxide as well as others for special purposes. Alumina, chromium oxide, zirconium oxide and zircon are often used to alter the fusion point of a composition.

Clays have been formed by the decomposition of rocks by various agencies through time. If the clay remains at the original location, it is a primary clay, usually white, with a low content of iron so that it "burns" white; it is called *kaolin* or *china clay*. It might be said that kaolins are the product of the weathering of feldspar—either potash feldspar, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, or soda feldspar, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$; the alkali has been washed away. They would then be termed primary clays, and this is true enough if the statement is qualified by adding that some kaolins, such as the Florida and Georgia kaolins, are transported, and hence are of secondary origin. If, in the course of geological changes, the clay has been transported (by water, glacier, or wind) to another location, it is a secondary clay [1]; it has lost the undecomposed, coarse particles of feldspar which remain in certain primary clays of that origin, but it now contains limestone powder, hydrated oxide mud, and organic impurities, in varying amounts. In general most of the clays other than white clays are of secondary origin, but there are exceptions here too, as for example the red-burning clays of Washington and Oregon, which have been formed by the weathering of basalt rock. The purer deposits of the secondary clays are more plastic than china clay, and are used under the name of *ball clays*.

The plasticity of a clay may be increased by aging, that is, storing it damp, or by exposing it to the action of the weather; the process is partly one of hydration accompanied by gelation, and partly a bacterial action which has as one of its results the further subdivision of the particles. Whiteware bodies are aged after filter-pressing by stacking the cakes one on top of another in damp cellars or bins. Clays are also washed for certain uses, and levigated to free them from coarse particles.

The analytical figures of some typical clays are given in Table 34.

The Manufacture of Whiteware

Whiteware, such as dinnerware, electrical porcelain, chemical porcelain, floor and wall tile, is generally made from a mixture of clays and other sub-

[1] River deposits are called fluviatile or alluvial, lake deposits lacustrine, and sea deposits marine.

TABLE 34.—*Typical analyses of clays.*

		Primary Kaolin[1]	Secondary Kaolin[2]	Ball Clay[3]	Shale[4]	Kaolinite[5]
Silica	SiO_2	44.2	44.7	53.3	58.0	46.5
Alumina	Al_2O_3	39.8	38.2	28.2	15.0	39.5
Iron oxide	Fe_2O_3	0.4	0.3	0.8	6.3	
Titania	TiO_2	0.1	1.2	1.7	0.6	
Lime	CaO	0.1	0.3	0.4	3.0	
Magnesia	MgO	0.3	0.2	0.5	2.7	
Soda	Na_2O	0.1	0.2	0.4	1.4	
Potassium oxide	K_2O	0.8	0.2	0.5	3.1	
Water*	H_2O	14.0	14.5	14.6	10.1	14.0

* Includes all loss on ignition.
1 An average North Carolina kaolin.
2 Typical Georgia kaolin.
3 Typical Tennessee ball clay.
4 Average of several red burning shales used for building brick and tile.
5 Theoretically pure kaolin $Al_2O_3 \cdot 2\ SiO_2 \cdot 2H_2O$.

stances. Usually these consist of kaolins [2] (china clay), ball clays, feldspar, and flint. The proportion of each of these depends upon the uses to which the ware will be put. Other materials which may be added to obtain special properties are talc (steatite), whiting ($CaCO_3$), or magnesite ($MgCO_3$), ground mica, finely ground alumina (Al_2O_3), zircon ($ZrO_2 \cdot SiO_2$), zirconia (ZrO_2) and beryl or beryllium oxide.

Processes of manufacture vary considerably in the various branches of the ceramic industry and within the branches themselves. A few examples of some of the broader branches will be given.

Dinnerware represents a large portion of the whiteware field; it is generally made by one of two methods, which are also used in other branches of porcelain manufacture; these are *slip casting* and *jiggering*.

Making the Slip. The proper amounts of the clays are weighed out and stirred in a blunger with water which may (but need not) contain electrolytes to disperse the clays until most of the lumps are broken up. The other substances, such as feldspar or flint, are then added and the whole stirred until thoroughly blended. The "slip," as the mixture is now called, is of a thin, creamy consistency and flows readily. It is allowed to run from the blunger through a vibrating screen, which removes bits of wood, metal, and lignite, and thence over a magnetic separator to remove iron particles which would stain the fired ware. The purpose of this is largely to remove impurities in the clays, and to get a uniformly blended mixture. Since the feldspar and flint are relatively pure, they are frequently held out at this point and added later.

Filtration and Aging of the Clay Body. From here, the slip flows to filter presses [3] where it is separated from the water and forms cakes containing 10 to 30 per cent of water. The cakes are stored in damp cellars where they are allowed to age, or they may be used immediately for making up the casting slip. As a general rule, only the body to be used for jiggering

[2] Kaolin is refractory, that is, it does not soften below 1700° C. [3092° F.] so that it is infusible at the kiln temperature; ball clay to hold water; flint for whiteness, rigidity, and to reduce shrinkage; feldspar as the flux or binder.
[3] Chapter 42.

is aged. The aging process improves the plastic properties of the clay body and insures even distribution of moisture in the mass.

In recent years washed air-floated clays have become available and some branches of the whiteware industry which do not require absolute whiteness have omitted the two steps of filtering and aging. These branches either make up the slip for casting directly in the blunger or after first dry-blending in a mixer. For jiggering the water is added at the mixer to give the desired degree of plasticity.

From this point on, the body is made into ware either by the casting process or the jiggering process.

Casting Process. The clay body from the filter cakes or aging bins, or the dry materials, if the first two steps can be eliminated, is placed in blungers with about 35 per cent of water and the proper amount of electrolytes, usually a mixture of equal parts of sodium silicate and sodium carbonate, in amount sufficient (for example, 0.1% of each on dry weight of batch) to give the desired fluidity to the slip. The clay body and water are thoroughly mixed, again screened (lawned) and run over a magnetic separator. The mixture now has the consistency of a not too heavy cream, and flows readily; it is termed the "casting slip" and is ready to use.

Molding the Casting Slip. The molds for forming the ware by the casting process are made of plaster of paris; they are so formed that the cavity in the mold has the shape or form of the ware to be produced. In order to allow for shrinkage during the drying and, later, firing of the ware, the mold is always made larger than the actual finished ware. In some types of ware, the oversize must be held to close tolerances.

The molds are filled with slip, and let stand for 15 to 30 minutes, or longer, depending on the desired wall thickness of the ware, and then the excess slip is poured out. The plaster of paris absorbs the water, and the clay body is left as a lining of the mold walls, exactly reproducing them. After the excess slip is poured off, the mold is allowed to drain, and is set for a period of 20 to 45 minutes in a warm place. At the end of this time the clay lining has set and shrunk sufficiently to allow its removal from the mold; the latter is used over again.

The normal products of slip casting are hollow ware, such as cups, pitchers and vases. Slip casting may be adapted, however, to the manufacture of solid pieces; for that purpose the slip is not drained but allowed to remain in the mold until it is set solid, the time often running to several hours. Slip must be added at intervals to replace the water absorbed by the plaster mold ("topping") and avoid a hollow center ("pipe").

Where heavy walls are required, as in some chemical porcelain articles, a plaster core is used, which forms the inside shape of the article.

The cast ware is then trimmed and dried in hot-air driers, after which it is fired. In some plants, and for some wares, a glaze coating is applied to the dried ware and both body and glaze are fired together. In general, however, a separate firing is given before and after glazing, known respectively as the bisque firing and the gloss firing.

Jiggering Process for Tableware. In making ware by "jiggering" or "jollying," the clay body from the storage bins is fed into a pug mill and tempered with enough water to give a stiff-mud consistency. From the pug mill it is forced by augers through a die in the form of a cylinder or "wad."

The "wads" are ready for use and are distributed to the jiggerman. The jigger consists of a rotating unit carrying a mold which will form one face of the ware while the tool forms the other face. For tea cups, which are made without handles (these are cast in "gangs" and fastened on later), the

FIGURE 65.—Cross-section through plaster of paris form for shaping clay cup.

mold forms the outside of the cup, and the tool the inside. For plates, the inner surface (later, the upper) is formed by the mold, and the bottom surface by the tool. Oval platters are made on a jigger having eccentric motion.

To make each object, a piece from the wad of just the right size is thrown on the center of the rotating mold and the tool brought down on it, spreading it over the mold and cutting away the excess clay. The tool is of metal and has a profile shape of the form desired on the surface it makes. During this operation the jiggerman keeps the clay-tool interface lubricated with water. The formed ware is placed with the mold in the drier. After drying, the ware is taken off and treated like the cast ware. The dry molds are returned to the jigger.

This process is much more rapid than the casting process and is used wherever the shape of the object does not prohibit it. It can be used for all simple shapes which contain no bulges or reverse curves.

The Saggers. In order to protect the ware from soot and dust during the firing, it is packed in clay boxes called saggers. Each box is open; they are piled on one another from the base of the kiln to the top, and the second box closes the first. The saggers are of various shapes and heights, to fit the ware. For example, one sagger can hold 4 piles of 20 plates each; the lowest plate rests on a thick form, the setter, which is used over and over; it prevents deformation of the lowest plate when it softens. The other plates are supported each by the next lower one, separated by flint granules, known as "bitstones."

The making of new saggers is a constant operation. The materials are broken saggers ground to a coarse grain, about 4 to 8 mesh, and fines; new clay, untreated in any way, and water. The mass is mixed in a pug mill, which cuts and mixes the dough-like mass, and discharges it into an extrusion machine which forces it out in the shape of a loaf of bread. This is cut in lengths of 16 inches or so, and one length is placed under a press which forms the saggers at one stroke between the descending die and a steel box. After firing, the saggers are ready to be used, and serve several times; when cracks in the side develop, they must be discarded. The use of saggers made of silicon carbide grain in place of fireclay grog is increasing.

The Pottery Kiln. The ware packed in the saggers is ready for the firing, which is done in one of a number of kilns, circular in cross-section, built of bricks, about 12 feet in diameter and 12 to 14 feet high inside. The kiln is built of common bricks outside, and of firebricks inside, and is surmounted by a stack. Each kiln has 6 to 8 small fireboxes at the base, whose fire gases enter the inner chamber at circumferential openings, and in addition at one central opening in the floor. To provide room for the fireboxes and necessary channels, the floor of the kiln is about 4 feet above the room floor (ground). The saggers are so arranged in the firing chamber that 5 "quarters" result, and within these quarters, the circulation of the fire gases may be regulated by means of empty saggers with suitable sections knocked off. A column of saggers set one on top of another in the kiln is called a "bung." The fire gases leave the kiln through a stack vent in the crown and from there to the stack proper, which surmounts the structure. By these means, the temperature may be so controlled that there is a difference of 15° F. (8° C.) between the top and the bottom. The heat is raised very gradually. The temperature at various points is observed by means of pyrometric cones (or Orton cones) sighted through peepholes at various levels. (See Chapter 46). The time of actual firing is about 66 hours; including cooling, unloading ("drawing"), and reloading, the cycle is 1 week. The maximum temperature is 2300° F. (1260° C.) for whiteware generally; porcelain may go to 2500-2550° F. (1371-1399° C.). At each packing the kiln is filled to capacity, about 2200 dozen pieces. The ware shrinks 10 to 15 per cent during firing, depending on the composition. The fuel is coal, gas,

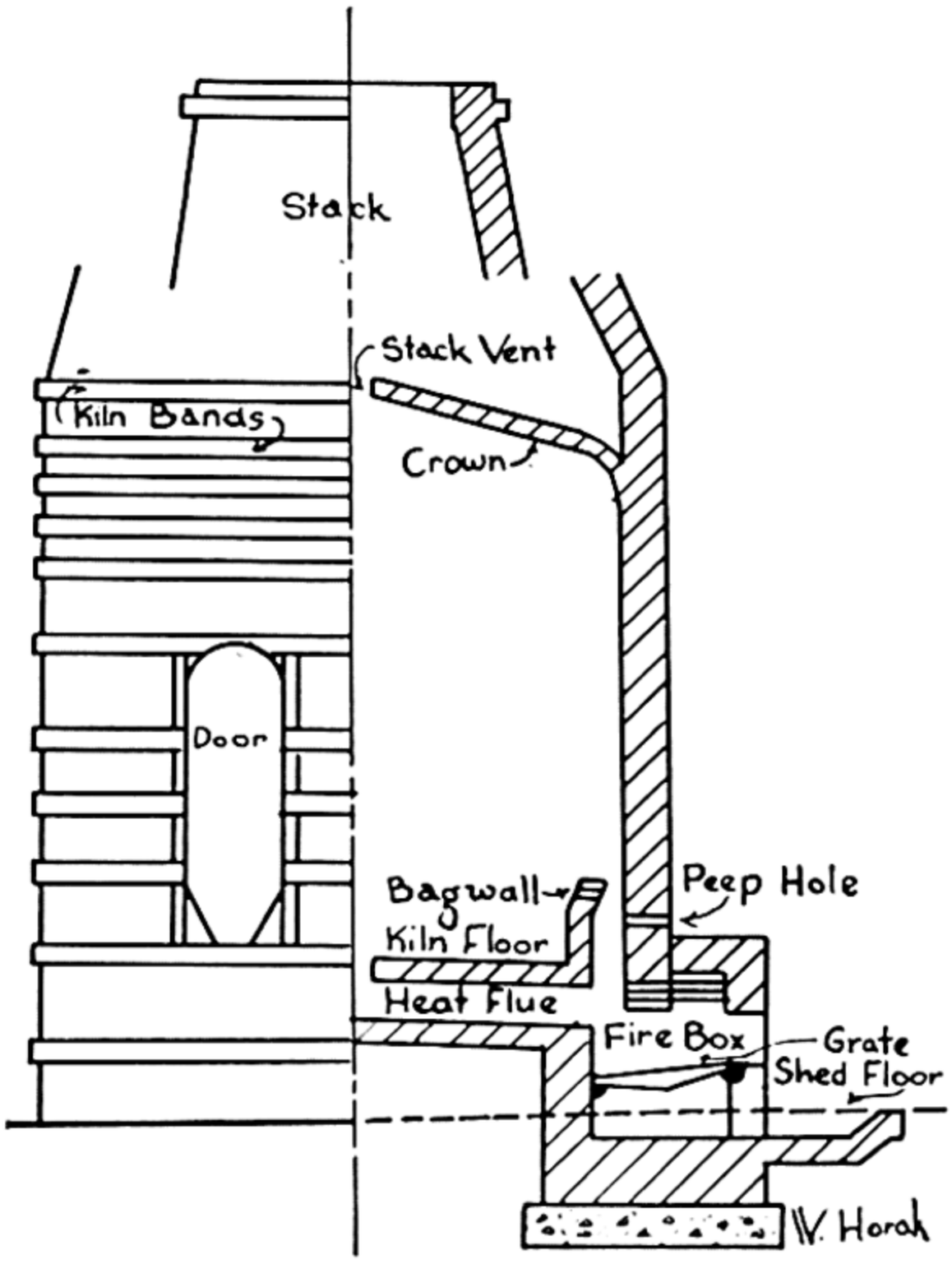


FIGURE 66.—Sketch of a typical pottery kiln. The ware is placed in saggers and these are set in the kiln in vertical rows called "bungs." The fire gases are directed upward by the bag walls in part, while another part is drawn to the center of the kiln by flues and ascends through the ware.

or oil, with coal the most common, but oil is a close second and gas is not rare, since the ware is high enough in price to allow the use of the more costly fuel.

Tunnel kilns in recent years have been replacing pottery kilns in the whiteware industry for both bisque and glost firing. Their continuous operation in comparison to the periodic operation of pottery kilns lends itself better to large-scale production.

The product from this first firing is the bisque ware, which is strong and hard; the second or glost firing is at a lower temperature and shorter. There are a few potteries which fire low at the first firing and high at the second.

A modified procedure has recently been developed which will have far-reaching, beneficial effects. The air remaining in the plastic clay, as it leaves the pug mills, is removed by the application of a vacuum. It is found that such de-aired products are stronger for a given thickness of wall than untreated ware, or as strong with a smaller wall thickness. Some clays which previously could not be used give satisfactory results when de-aired. The same wall thickness, with firing at a lower temperature than previously, gives as strong a ware.[4]

Decorating and Glazing. For under-glaze decorations, the bisque is brushed with shellac, and the pattern transferred to it by means of decalcomania paper. The pigments are so selected that the color obtained after firing is the desired one; the first color from the transfer paper is immaterial. Very elaborate designs covering the whole plate in some cases may be applied by means of decalcomania paper. Hand painting and a combination of decalcomania and hand painting are also practiced. The decalcomania paper may be made in the pottery itself, from an etched plate coated by the proper pigments, and applied to a strong but thin paper first treated with a soap solution.

The decorated pieces are passed into a suspension of the glaze; they retain enough to cover them. Next they are dried and packed in saggers again, but this time they must not touch; they rest on three pegs set in the wall of the sagger.[5] The saggers are fired at a lower temperature for 30 hours only. The glaze is more fusible than the bisque and no deformation takes place. Overglaze decoration is less durable.

The glaze must be transparent for underglaze decoration, and must not react with the colors of the decoration so as to change the shade, or cause them to run together; it may be opaque for overglaze decoration; it must have approximately the same coefficient of expansion when heated as the under body, so that it will not "craze" or peel off. One formula includes sodium oxide, borax, zinc oxide, silica, tin oxide, calcium carbonate, and lead oxide; it produces an easily fused, non-transparent, white glaze.

There are various kinds of tableware bodies; the more important ones are

[4] "The effect of de-airing stiff-mud bodies for clay products manufacture," by J. O. Everhart, C. R. Austin, and W. C. Rueckel, *Ohio State University Studies, Engineering Series, Bull.* 74 (1932); in cooperation with the Bonnot Co., Canton, Ohio.

[5] The marks of the three pegs may be seen on the under side of almost any plate.

real porcelain, strong and non-porous (ink makes a slight stain); semi-porcelain, less strong, somewhat porous (ink makes a deep stain).

Stoneware is made from clays not selected for color, although in some cases the color is pleasing; it is fired at a temperature approaching that at which porcelain is fired. The ware is not packed in saggers, and the glaze is applied by means of salt, introduced at the top of the fire in the firebox toward the end of the firing period. Sewer pipe and glazed conduit are "salt glazed" in the same way. The salt melts and volatilizes, condenses on the ware and attacks its surface just enough to make it run. Stoneware is cheaper than porcelain, except in a few cases when for artistic merit the ware brings as much as porcelain. Earthenware has a porous body; it is

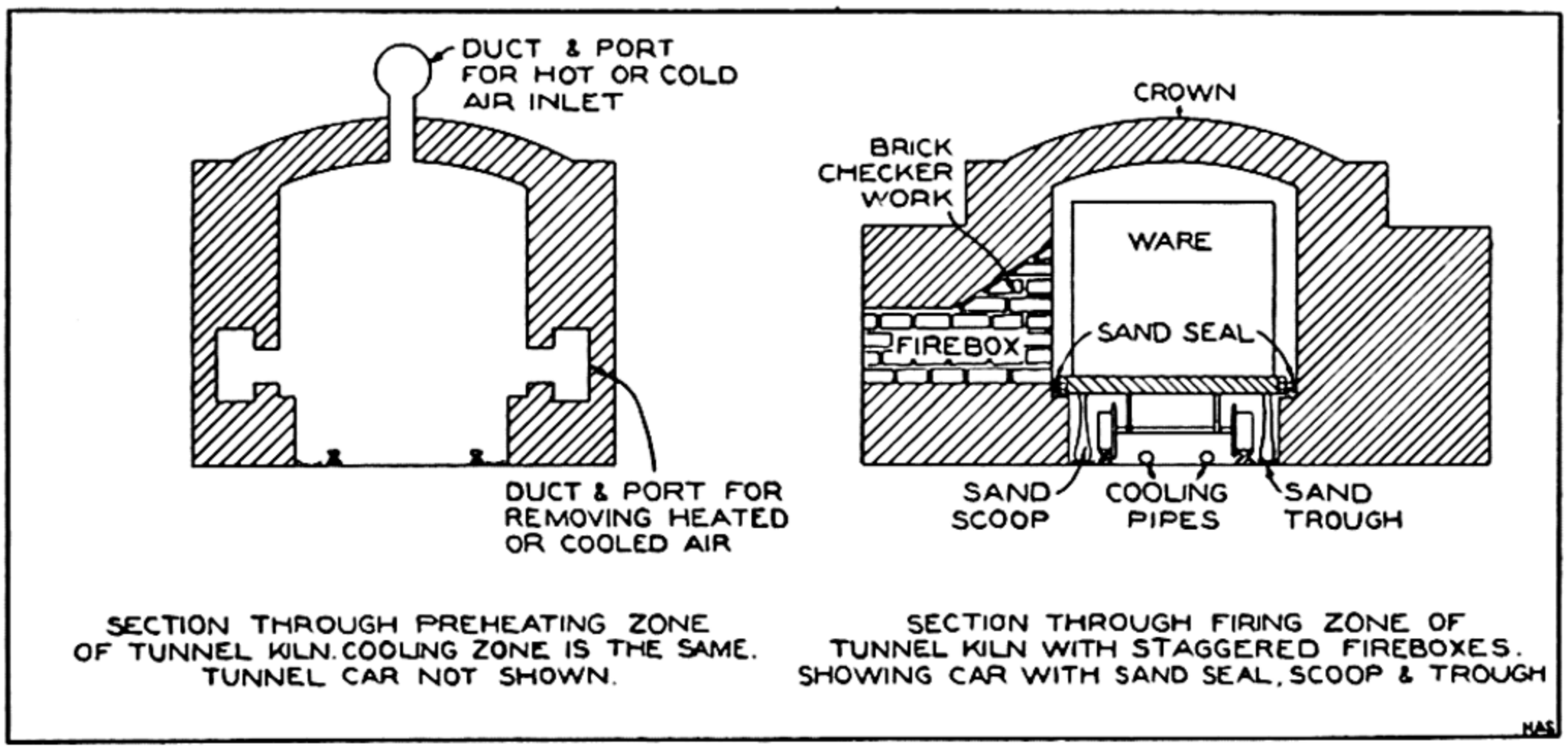


FIGURE 67.—The tunnel kiln, as used in ceramics.

fired at moderate heat, insufficient to cause complete vitrification; if the ware is to be water-tight, it must be glazed. There are many products which occupy intermediate places, so that a classification is difficult. Chemical stoneware is generally brown in color, and fired without saggers, but it is made with great care. Certain pieces such as the Cellarius vessel [6] have surprisingly thin walls, so that cooling may be rapid; yet they are strong. Other pieces are used chiefly for storage of acids, and are as large as 6 feet in height; the walls are then made thicker.

Electrical insulators of the umbrella type, for high-tension currents, are made of a clay mixture similar to the kind used for fine tableware. A large unit is about 10 inches across and 6 inches high; it is shaped in a mold for its one side, and with a tool on the jigger wheel for the other. The units are dried, packed in saggers, loaded on kiln cars, and fired in a tunnel kiln.

The insulator units are glazed. After firing, they are tested for resistance to high-voltage current, as well as in a number of other ways. Twenty units set up one in the other offer enough resistance to prevent a million-volt current from passing.

During World War II new porcelains containing high percentages of zircon and zirconia were developed having special desirable properties.

[6] Water-cooled stoneware vessel formerly much used for cooling chlorine gas.

Also bodies with high titania content have been perfected for their special dielectric properties. The whiteware industry made a major contribution to the war effort by producing non-magnetic pottery land mines. In other directions, ceramics plants played an important role in supplying the armed forces; for example, one plant in the East installed an entirely new working force in specially erected buildings to manufacture thousands of insulators for the Signal Corps.

Tunnel Kiln. The tunnel car kiln is aptly named, since it is a tunnel built of firebrick through which cars carrying the ware to be fired are made to travel. It is divided into three zones; (a) the preheating zone, where the cars enter and the ware is preheated by waste heat from the cooling zone;

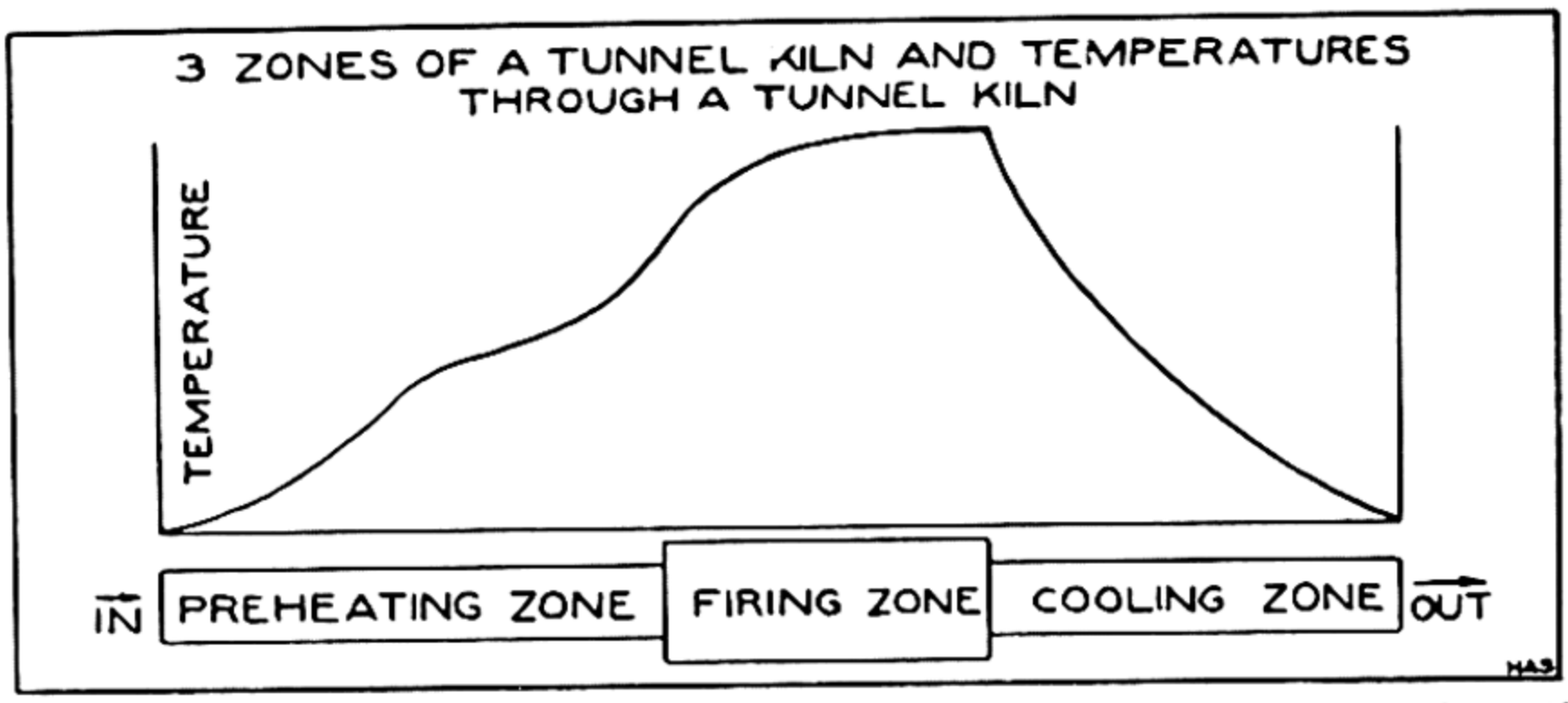


FIGURE 68.—The heating, firing and cooling zones in a tunnel. The temperature designation is left out purposely, as it will differ for the several wares.

(b) the firing zone, wherein the ware is brought to the desired temperature; and (c) the cooling zone. The firing zone portion is the only zone equipped with fireboxes, and it is wider than the preheating or the cooling zone for that reason. The usual fuel is oil, but coal, gas, and even electricity have been used successfully. In the cooling zone, outside air is introduced at the top exit end and drawn by fans through the ware to a point near the firing zone where they are exhausted at the sides at a point about level with the car tops. The air thus heated by the ware is carried by pipes to the preheating zone where it can give up its heat to the incoming ware.

The size of tunnel kilns varies considerably; the length depends upon the particular ware to be fired, especially upon the size of the individual pieces. Larger pieces require a longer kiln. Tunnel kilns have been built as much as 400 feet long and as small as 24 feet long. The length of the zones depends on two considerations: the length of the kiln, and the particular heat treatment the ware may require.

Not only straight tunnel kilns, but circular ones are built; in the latter, the entrance end is close to the exit end.

The cars are moved through the tunnel by various types of "pushers"—rams operated hydraulically, pneumatically, or mechanically—or by a chain under the cars.

The tunnel kiln is used for all kinds of ceramic products, not merely for

electrical insulators. It has come into favor because it saves labor, packs faster, saves heat, and even more important, because the temperature prescribed is more definitely reached for uniform periods over all of the ware—that is, the firing is more uniform. Let it be emphasized again that the operation is continuous rather than periodic.

Color and Luster. Iridescent ware (luster ware) is produced by exposing the hot ware to the vapors of stannous chloride or ferric chloride. Iridescence combined with color is produced by applying a mixture of silver sulfide and clay, and exposing to a smoky (reducing) flame.

Gold gives its characteristic color over the glaze. In general the decorating colors are not simple oxides but complex calcines. The colors which some metal oxides give when used in the glaze are listed below. It is worth noting that the famous chinese red glazes are colored with copper.

Cobalt oxide produces various shades of blue
Copper oxide produces greens and reds
Chromium oxide produces greens and reds
Iron oxide produces yellow to brownish red
Uranium oxide produces yellow to orange red
Gold chloride produces pinks
Manganese oxide produces shades of violet

Building Bricks

The familiar red brick is made from a secondary clay containing in the neighborhood of 4 per cent iron oxide as a natural impurity. If the clay is highly plastic, sand is usually added, but finely crushed rock may be used to reduce the plasticity, which would lead to excessive shrinkage, cracking and warping. For the cheapest good bricks, the dry material must pass through an 8-mesh screen; for finer grades, a 20-mesh screen. The density of the brick depends mainly upon the method of working; a wire-cut brick, not re-pressed, would be the lightest; on placing it in a mold and pressing it by a screw-operated die, it becomes denser, as well as more accurate; power pressing will raise the density still further.

Stiff-mud Process for Heavy Clay Products. This process is widely used for making building brick, tile, paving brick, some terra cotta, conduit, drain tile, and for some types of firebrick. A variation of the process here described is used for making most sewer pipe.

The clay as it comes from the pit or storage bins is ground in dry pans and carried to a pug mill, where it is tempered with the proper amount of water to give a stiff, mud-like consistency. From the pug mill it is forced by an auger screw through a steel die of the shape desired for the finished ware. The clay issues from the die head as a continuous column. A few feet from the die head, a cutter, generally automatic, consisting of piano wires set at proper distances on a jig (movable frame), cuts the column into the right lengths. The cut raw ware continues on a belt conveyor, from which it is picked and set on a drier car. Full cars of bricks, with 1,000 to 2,000 bricks per car, are pushed into driers and left to dry according to a predetermined schedule for the particular clay used. From

the driers, the cars are taken to the kiln yard; the dry ware is taken off and set in the kiln, usually of the down-draft type, for firing.

The Round Down-draft Kiln. The down-draft kilns are built as large as 40 feet in diameter and 12 to 19 feet from the floor to the top of the crown. The one shown in Figure 69 has eight fire boxes around its circumference. The heat and combustion gases from the fire boxes are directed upward toward the crown and are reflected by the crown downward through the ware; the gases pass through slots in the floor into the collecting flues and center well hole, and finally through the main flue to the stack. The

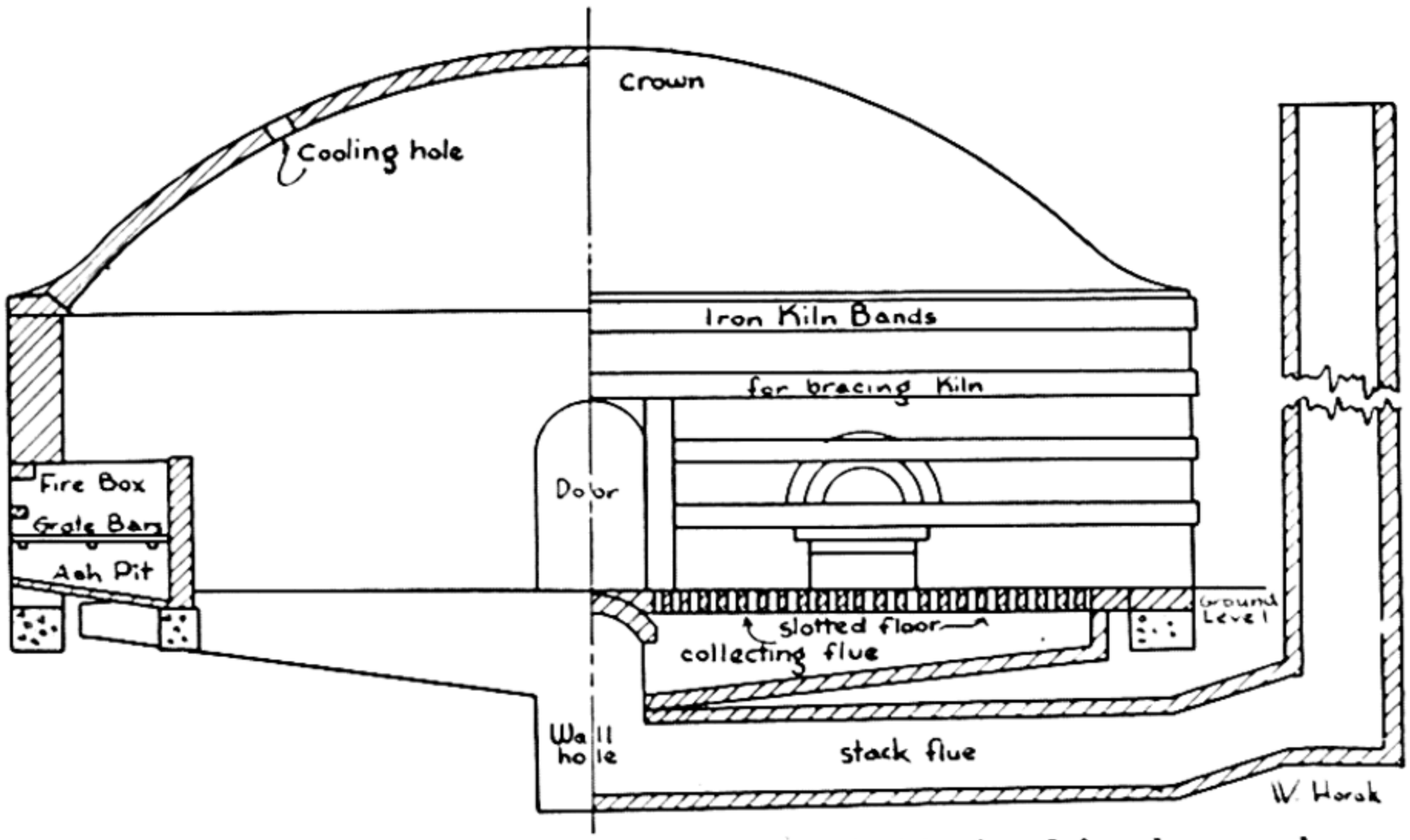


FIGURE 69.—The round down-draft kiln, suitable for firing heavy clay products. (See text.)

firing temperature varies considerably; in the case of a dense red brick, for example, the maximum temperature will lie between 1470° and 1650° F. (800° to 900° C.).

By careful setting of the ware and skillful firing, the temperature distribution may be made uniform throughout. This type of kiln is periodic in operation; it is fired by coal, oil, or gas, but mostly by coal.

After firing, the bricks are sorted; those with perfect shape, color and correct dimensions are No. 1 bricks; less perfect ones are grouped together as seconds; insufficiently burned ones are added to the new charges. The price of wire-cut red bricks, of first quality, is about $20 to $35 a thousand.

FIREBRICKS

Firebricks are the material for the construction of open-hearth steel furnaces, for iron and other blast furnaces and stoves, for cupolas, calciners, and many other types of chemical engineering apparatus; they serve to line fireboxes and furnaces, and to fill regenerators. The materials are a fireclay made even less plastic than it normally is by preliminary firing at high temperature followed by crushing and known as "grog"; and a smaller proportion of a more plastic fireclay to furnish the bond. The firing is done

at a temperature of 2500° F. (1371° C.) to 2850° F. (1565° C.) for super-duty brick. In special cases the firing temperature may be as high as 3000° F. (1650° C.) or somewhat higher. The burned bricks are cream-colored, light buff, or almost white, depending on composition and firing. They vary in hardness and porosity depending on their use. Firebrick costs about $45 per thousand, for low heat-duty brick, up to as high as $1250 for some high-grade super-duty brick.

There are many kinds of refractories; the primary objective of them all is to confine heat, and at the same time to resist the attack of metals, slags or glass at high temperatures without appreciable distortion or softening. Another objective is to produce a refractory for high-temperature insulation; such insulating refractories do not resist abrasion and slagging. They can be used as refractories where these properties are not required; usually they are used as an insulating backing to a first course of the more slag- and abrasion-resistant brick. Insulating refractories are generally light in weight and mechanically weak and soft.

The nature of the raw materials depends upon the intended use; silica is selected for bricks which must be resistant to acid slags, but silica bricks are also used for heat conducting, in by-product coke ovens, for instance. Basic bricks, which resist basic charges, are made of magnesia, bonded only by water under great pressure, or by bauxite or alumina. The plants built during the war for extracting magnesium from sea-water have produced magnesia for refractories. This use will probably increase in the near future.

There are also neutral bricks, such as chromite, graphite, and silicon carbide. In metallurgy, the nature of the slag determines the class of refractory to be used; thus a siliceous slag requires an acid refractory. For crucibles which must conduct heat as well as resist high temperature, natural graphite[7] bonded with 30 per cent clay and some water glass is largely used. Silicon carbide bonded with lime serves for muffles and electric furnace linings; clay-bonded silicon carbide is the general choice for high heat-conductivity brick; with graphite in addition, the mass becomes sufficiently elastic to form crucibles. An excellent high-conductivity crucible is made from silicon carbide[8] and tar; the carbon residue from the latter becomes the bond and is prevented from oxidizing during use by a glaze. Clay pots are used in the glass houses; they are purchased unburned by the glass maker, who must burn them in his own furnaces.[9]

The highest-grade silica bricks are made of quartzite or ganister, and bonded by 2 per cent lime; they are generally heated twice, because they expand when heated (fireclay bricks shrink), and it is desirable that the expansion be complete before the wall or lining is built. The expansion is due to the change of quartz into cristobalite and tridymite, which are less dense forms of silica.

Much harm can be done by too rapid heating of the bricks in the process of manufacture; and the gradual cooling is just as important, for too rapid cooling causes strain and weakens the bricks. The same applies

[7] Formerly Ceylon graphite; now largely Madagascar graphite.
[8] U. S. Patent 1,356,939.
[9] Chapter 11.

TABLE 35.—*Pyrometric Cones (Originally Known as Seger Cones)*

Table of Fusing Points

Cone Number		When fired slowly 20° C. per hour		When fired rapidly 150° C. per hour	
		° Cent.	° Fahr.	° Cent.	° Fahr.
Heavy Clay Products — Decoration	022	585	1085	605	1121
	021	595	1103	615	1139
	020	625	1157	650	1202
	019	630	1166	660	1220
	018	670	1238	720	1328
	017	720	1328	770	1418
	016	735	1355	795	1463
	015	770	1418	805	1481
	014	795	1463	830	1526
	013	825	1517	860	1580
	012	840	1544	875	1607
	011	875	1607	905	1661
	010	890	1634	895	1643
	09	930	1706	930	1706
	08	945	1733	950	1742
	07	975	1787	990	1814
	06	1005	1841	1015	1859
	05	1030	1886	1040	1904
	04	1050	1922	1060	1940
Art Pottery	03	1080	1976	1115	2039
	02	1095	2003	1125	2057
	01	1110	2030	1145	2093
	1	1125	2057	1160	2120
	2	1135	2075	1165	2129
	3	1145	2093	1170	2138
Whiteware	4	1165	2129	1190	2174
	5	1180	2156	1205	2201
	6	1190	2174	1230	2246
	7	1210	2210	1250	2282
	8	1225	2237	1260	2300
	9	1250	2282	1285	2345

Cone Number		When fired slowly 20° C. per hour		When fired rapidly 150° C. per hour	
		° Cent.	° Fahr.	° Cent.	° Fahr.
Electrical Porcelain	10	1260	2300	1305	2381
	11	1285	2345	1325	2417
	12	1310	2390	1335	2435
	13	1350	2462	1350	2462
	14	1390	2534	1400	2552
Refractories	15	1410	2570	1435	2615
	16	1450	2642	1465	2669
	17	1465	2669	1475	2687
	18	1485	2705	1490	2714
	19	1515	2759	1520	2768
	20	1520	2768	1530	2786
	23			1580	2876
	26			1595	2903
Clay Testing (PCE)*	27			1605	2921
	28			1615	2939
	29			1640	2984
	30			1650	3002
	31			1680	3056
	32			1700	3092
	33			1745	3173
	34			1760	3200
	35			1785	3245
	36			1810	3290
	37			1820	3308
	38			1835	3335
	39			1865	3389
	40			1885	3425
	41			1970	3578
	42			2015	3659

* Pyrometric Cone Equivalent.

to refractories in use, and care should be exercised in both heating and cooling furnaces.

For some years, refractories have been produced in the electric furnace.[10] In recent years these have found extensive use in the glass industry; since the war their use is extending into other industries, particularly where high resistance to abrasion and slagging are of prime importance. (Compare next chapter.)

The fireclay refractories, priced at $45 to $75 a thousand (with shapes computed to the standard $9'' \times 4\frac{1}{2}'' \times 2\frac{1}{4}''$ brick), made up 75 per cent of all refractories; their distribution is 35 per cent to boiler linings and locomotives; 20 per cent to open hearth steel furnaces; 10 per cent to heat-treating furnaces and the like; 4 per cent to the glass industry; 4 per cent to the ceramic industry. The composition varies considerably, from silica brick (95 to 98 per cent silica) to highly aluminous brick (92 per cent alumina). Fireclay brick will vary from 55 per cent silica and 35 per cent alumina to 55 per cent alumina and 40 per cent silica; the balance consists of accessory oxides in the clay. The "sillimanite" refractories, now used quite extensively, approximate a composition of 63 per cent alumina and 34 per cent silica.

Refractories are tested for the temperature of deformation under load, linear shrinkage on heating, resistance to spalling on repeated heating and sudden cooling, and resistance to three types of slag. A few further particulars will be found in Chapter 45.

In firing ceramic wares, the rate of temperature increase is observed by means of thermocouples. The finishing temperature, however, is most commonly determined by means of *pyrometric cones*. Thermocouples and pyrometric cones are fully described in Chapter 46. A table for the latter prepared with special reference to the firing of ceramics is adjoined.

Vitrified Enamel or Porcelain Enamel*

"Vitreous enamel or porcelain enamels are fused silicate coatings applied to metal (usually cast iron or sheet steel).

"The first step in all types of vitreous enameling is the making of the 'frit.' Proper proportions of raw materials such as feldspar, borax, soda ash, silica, fluorspar, cryolite, sodium nitrate and the like are thoroughly mixed and then fused in a smelting furnace. The melt is drawn off into water and the resulting friable product is termed 'frit.'

"The application of the enamel is accomplished by two general methods, the wet and dry process. In the former method the frit is ground in a pebble mill in the presence of water and clay to produce a workable suspension, or 'slip.' Opacifiers and coloring oxides are also added in the milling.

"The ware to be enameled by the wet process, after proper fabrication and cleaning, is coated by dipping it in the milled enamel followed by draining off the excess, or by spraying the slip onto the ware. In either case the

[10] Fred W. Schroeder, *Ind. Eng. Chem.*, 23, 124 (1931).

* The quoted portion is the statement prepared especially for this chapter by Mr. Emerson P. Poste, Consulting Chemical Engineer, Chattanooga, Tenn.

enamel coating is dried and then fused in an enameling furnace. One or more coats are thus applied as may be required. The coat applied directly on the metal is usually of a special nature [11] to promote a firm adherence, while subsequent coats develop the desired color and texture.

"For application by the dry process, dried frit is ground to a fine powder in a dry mill, with the addition of the proper coloring oxides and opacifiers. The piece to be enameled receives a first coat by the wet process. The burnt first coat is not allowed to cool, however, but while the article is still hot the dry ground enamel powder is applied by means of a sieve. The piece of ware is then replaced in the furnace and the coat fused. Two or more such applications are usually required to produce the desired results.

"Cast iron sanitary ware is usually produced by the dry process, most other ware by the wet process.

"Formerly all enamel plants produced their own frit. More recently large supply houses have marketed increasing amounts of frit to the smaller, and many of the larger enameling concerns. The frit as purchased by the enameling plant is ready for milling. Most of the frit thus purchased is for wet process enameling, in accordance with the above method.

"There is an increasing demand for enameled commodities as the merits of vitreous enamel become better recognized in a great variety of uses. Formerly the chief outlet was in the form of sanitary and cooking ware. Then came vitreous-enameled signs, stoves, refrigerators and dairy, canning and chemical equipment. The present rapid expansion involves a multitude of uses including parts for buildings. The future possibilities are almost unlimited.

"The following may be taken as a typical white enamel for sheet iron:

White Frit	Per cent	Mill charge
Feldspar	29.5	
Borax	22.0	100 lbs. Frit
Silica	19.0	6% Clay
Cryolite	13.5	5% Tin oxide
Soda ash	3.5	
Fluorspar	3.5	
Sodium nitrate	3.0	
Antimony oxide	3.0	
Zinc oxide	3.0	

"As to colors, certain general facts may be stated: Red colors are usually made from iron, cadmium and selenium compounds. Greens are made from chromates or chromates properly combined with other mineral oxides. Yellow is produced from compounds of antimony, uranium and titanium. Blues are usually based on cobalt compounds, in combination with other mineral oxides to vary the color.

"There are three general ways of producing the desired colors. For the darker blues and black, coloring oxides are usually smelted in the frit. For certain other colors a relatively clear frit or glaze is used, the color and opacity being produced by mill additions. For the more delicate an opaque

[11] A ground coat is applied to cast iron and sheet iron, and fired; it must contain cobalt to promote the adherence to the metal surface; it is then dipped or sprayed with the cover coat, and fired once more (firing time 3 to 7 minutes). E. R. R.

frit, such as given in the formula above, is used, and coloring oxides and varying amounts of opacifier are added at the mill."

Porcelain enameled wares are pushing into new fields constantly. Thus, porcelain enameled chutes have been introduced in coal handling equipment, where they provide not only a higher rate of flow, but furthermore wear less fast than steel chutes. Grain chutes and package chutes similarly are porcelain enameled to advantage.[11a] Porcelain enameled aluminum clapboards for dwellings are coming into favor; they require no painting.

The production of unglazed brick in 1946 amounted to 4.9 billion bricks, more than twice as much as in 1945, yet only half as great as in the peak year of 1925. The production in 1947 was similar to that of 1946. In March, 1948, the production was 389 million unglazed bricks for the month. The value in December, 1946, was just under $21 a thousand bricks; in February, 1948, it was $23.

China tableware produced in the United States in 1946 amounted to 11,289,000 dozen pieces, valued at $32,816,000; in the first half of 1947 5,891,000 dozen pieces were produced, valued at $20,139,000.

Fireclay refractories shipped by manufacturers in the United States during 1945 were valued at $66.1 million; included in this total are 521.5 million units of 9-inch equivalent fireclay brick and standard shapes valued at $32.3 million.[12]

Other Patents

U. S. Patent 1,844,670, manufacture of an improved vitreous, acid-resisting enamel; 1,785,777, preparation of a slip for vitreous enamels consisting of an acid-resisting glass, titanium sulfate, and English pipe clay; 2,048,319, producing cast refractories; 2,069,059, method of producing ceramic ware; 2,235,881, acoustic tile; 2,207,911, mixture for vitrified ware; 2,230,206, dinner ware. Apparatus for feeding clay to mold in the manufacture of pottery ware, U. S. 2,421,572. Ceramic dielectric composition, U. S. 2,420,692; dielectric composition having controllable capacity temperature coefficient comprised of titanates and the alkaline earths. Aluminum phosphate bonded diamond abrasive, U. S. 2,420,859; an article composed of diamond grains and a ceramic bond. Alumina low silica refractory, U. S. 2,424,082; refractory made by casting the molten materials into special forms; refractory composed of crystals in an amorphous matrix. Manufacture of an improved vitreous material U. S. 2,032,239; an electrically insulating material compound of mica and frit. Cast refractory products; U. S. 2,416,472; refractory product formed by casting a molten mixture of magnesia, zirconia and alumina in special molds.

Problems

1. A kiln packed with saggers contains in all 2200 dozen pieces of tableware. Each piece weighs ½ pound, and there are required 3 pounds of coal for each pound of ware fired. How many tons of coal are needed in all? With coal at $6.00 a ton, what is the fuel charge against each dozen pieces?

2. A ware is made from a clay mixture which contains exclusively china clay, flint and feldspar. The feldspar in the batch is 22.5 per cent on the dry basis. The final ware contains 68 per cent SiO_2. Taking the formula in the text as the composition of the feldspar, the composition of the china clay in the text as applying, and the flint as 100 per cent SiO_2, how much of each raw material would you have to take, for each 100 pounds of ware?

3. It is required to smelt 2½ tons of frit for a white vitrified enamel of the formula

[11a] "Utilization, the magazine of coal uses," Aug. 1948, p. 25.

[12] "Facts for Industry."

given in the text. Assume a loss from all sources of 5 per cent. How many pounds of each of the materials listed will be required, if the loss is spread over all the items uniformly? It must be remembered that sodium nitrate and soda ash lose gases during the smelting as a normal reaction; in finding the theoretical yield, which must be done first, sodium nitrate and soda ash should be changed to their sodium oxide equivalent.

Reading References

"Properties of some European plastic fire clays," A. V. Bleininger and H. G. Schurecht, *Bur. Standards Tech. Paper* **No. 79**, Washington (1916).

"Constitution and microstructure of porcelain," A. A. Klein, *Bur. Standards Tech. Paper* **No. 80**, Washington (1916).

"Modern Brickmaking," Alfred B. Searle, London, Scott, Greenwood and Son, Ltd., New York, D. Van Nostrand Co., 1911.

"Manufacture and properties of sand-lime brick," W. E. Emley, *Bur. Standards Tech. Paper* **No. 85**, Washington (1917).

"Materials and methods used in the manufacture of enameled cast-iron wares," Homer F. Staley, *Bur. Standards Tech. Paper* **No. 142**, Washington (1919).

"Enamels for sheet steel," Robert D. Landrum, *Ind. Eng. Chem.*, **4**, 561 (1912).

"Carborundum refractories," S. C. Linbarger, *Ind. Eng. Chem.*, **10**, 847 (1918).

"Recent development in ceramics," A. V. Bleininger *Ind. Eng. Chem.*, **10**, 844 (1918).

"Electric-furnace production of high-heat-duty refractories," Fred W. Schroeder, *Ind. Eng. Chem.*, **23**, 124 (1931).

"Corrosion problems in the rayon industry," Percy C. Kingsbury, *Ind. Eng. Chem.*, **22**, 130 (1930), on stoneware installations.

"Clay technology," Hewitt Wilson, New York, McGraw-Hill Book Co., 1927.

"Enamels," A. I. Andrews, Champaign, Illinois, 1935.

"Refractories and their applications," W. F. Rochow, *Trans. Amer. Inst. Chem. Eng.*, **31**, 228 (1935).

"Recent developments in manufacturing and using refractories," Louis J. Trostel, *Chem. Met. Eng.*, **42**, 363 (1935).

"De-airing in the auger machine without vacuum pump," W. D. Richardson, *Bull Am. Ceramic Soc.*, **16**, 14 (1937).

"The manufacture of ceramic decalcomania," G. H. Stapleford, *Bull. Am. Ceramic Soc.*, **15**, 335 (1936).

"A new inorganic cement and adhesive," Dean S. Hummel, *Ind. Eng. Chem.*, **29**, 123-131 (1937).

"Ceramics and chemistry," Percy C. Kingsbury, *J. Chem. Ed.*, **9**, 795 (1932).

"New stoneware in electrochemical field," Percy C. Kingsbury, *Trans. Electrochem. Soc.*, **73**, 303 (1939).

"Structural clay products," J. Joseph W. Palmer, Trade Inf. Bull. 842, Bureau of Foreign and Domestic Commerce (1939).

"Pottery Production Processes." J. J. Svec. Industrial Publications, Chicago, Ill., 1946.

"Refractories," 2nd Ed., F. H. Norton, McGraw-Hill Book Co.

"Clays—deflocculation and casting control," G. W. Phelps, *Ceramic Age*, (5) 1947.

"Reactions occurring in decoration of vitrified chinaware using underglaze decalcomania method," A. M. Flanigan, *J. Am. Ceram. Soc.*, **30**, (4) 125-129 (1947).

"Vermiculite insulating brick," R. F. Rea, *Amer. Ceram. Soc. Bull.*, **26**, (2) 36-38 (1947).

"Ceramic Whitewares—History, Technology and Applications," Rexford Newcomb, Jr., Pitman Pub. Corp., 1947.

"Applications of super-refractories made from electric furnace products," C. F. Geiger, A. A. Turner, and O. R. Stach, *Chem. Eng. Progress*, **44**, 933 (1948).

"New alumina-silica refractories," G. B. Remmey, *Chem. Eng. Progress*, **44**, 943 (1948).

"Let there be light," said the Lord, and there was light. It was left to man to devise a way to let the precious gift enter the shelter of his house to dispel the darkness. So he invented glass, and as the years went by, the panes for his windows were made larger and larger. Now glass serves him generously, in many, many ways. Consider the picture window in the suburb, the daylight wall in the factory and store, the safety glass in the automobile. Light may enter almost wherever we go.

Chapter 11*

Structural Glass, Glass Containers, Optical Glass, Special Glass

The history of glass reaches as far back as the known history of man. In the tomb of Tutankhamen, who came to the throne in 1358 B.C., Mr. Howard Carter and Lord Carnarvon found a head-rest of glass; objects made of inlaid colored glass; and two figures in glass, the bodies in red and wigs in dark blue. Tablets dating from 600 B.C., during the reign of Assurbanipal, King of Assyria, describe glass-making materials and furnaces. Until the first century B.C., glass served for making ornaments; it was in this century that the glass maker's blowpipe was invented, and with it, the blowing of glass into molds. With this discovery, glass became an object of utility as well as of ornament. From Egypt, Assyria and Syria, the art spread to Rome and the Roman world, as indicated in Figure 70.

In the Roman period a high standard of technical skill and beauty of form was reached. The Roman artisans made drinking glasses, bottles, jars, basins, windows and vials; in the working of glass they practiced twists, loops, threads, cutting in depth, cutting in relief, gold inlay and engraving. With the fall of Rome, 475 A.D., the civilization that had been developed by Rome declined and with it the arts and handicrafts, including glass making. However, the latter continued to be practiced in the area between the Rhine and the Seine, as well as in Normandy and Spain. In the period from the 7th to the 11th century, activity was diverted from vessels to sheet glass for the glazing of churches and cathedrals.

In the Eastern Roman empire the glass-making art flourished, as attested by the large and numerous mosaics made up of colored and gilt glass in the great church of St. Sophia, built in the period of 532 to 538 A.D. by Justinian.

In Western Europe, with the rise of the Republic of Venice (around 1071 A.D.) glass for utility and ornaments became an important article of manufacture and trade. The traditions of Constantinople, Syria and Egypt formed the basis of the Venetian industry in glass. The Venetians made vessels, mirrors, lace glass (Vitro de trina), frosted glass, aventurine glass, glass spectacle lenses, and "crystal glass." The glass furnaces were originally within the city, but were moved in 1291 to the island of Murano nearby, because of the fire hazard. Glass-making was a state monopoly for many centuries. In the 17th century the glory of Venice waned, and pre-

* In collaboration with Donald E. Sharp, Assistant Director of Research, and Alfred E. Badger, Research Supervisor, Libbey-Owens-Ford Glass Company, Toledo, Ohio.

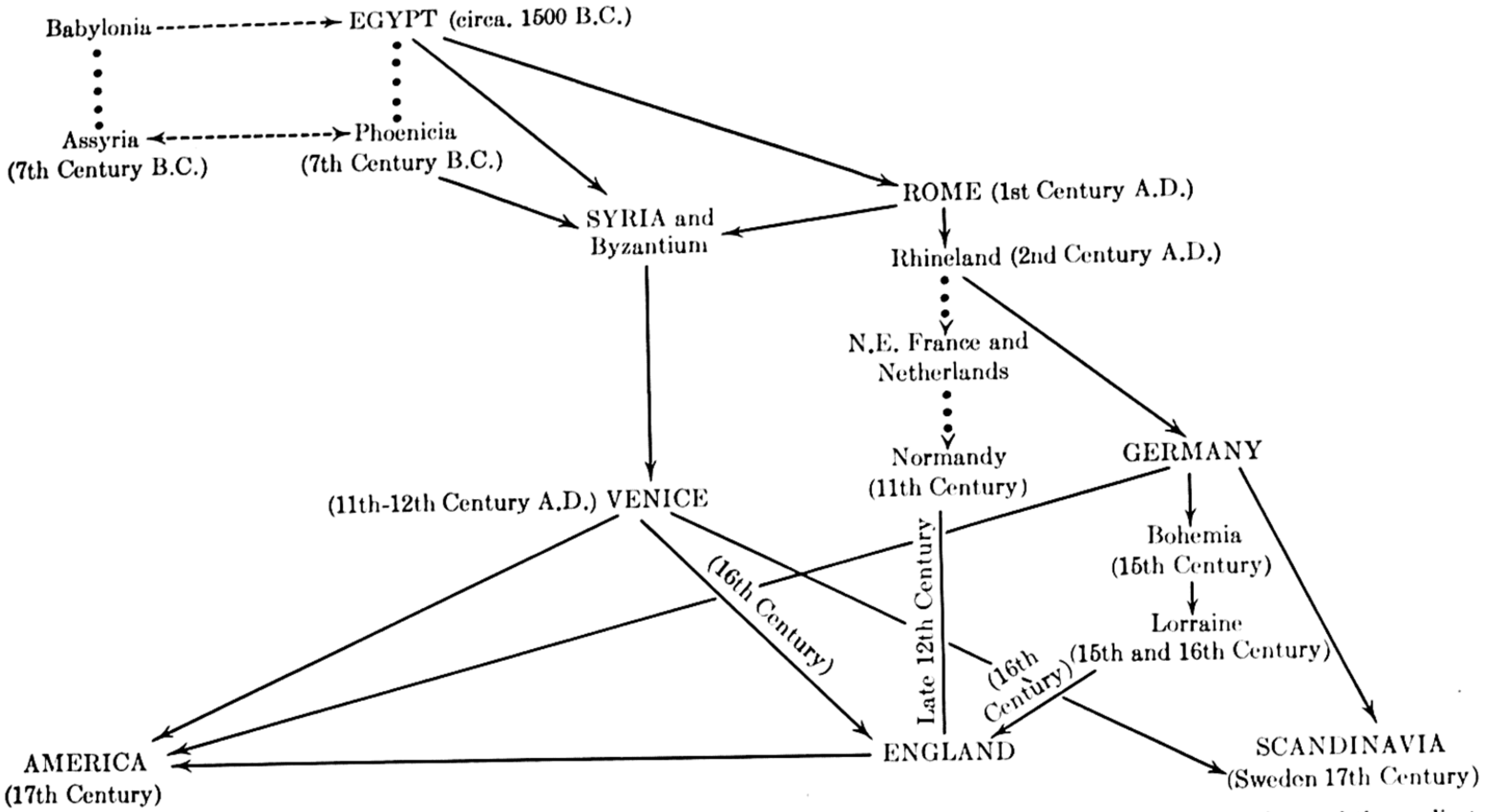


FIGURE 70.—The origin and main streams of the northward and westward spread of glassmaking. The dates are those of the earliest established records. The initial date on the chart refers to the making of glass vessels. Note: ———— ascertained fact of reasonable certainty; ····· reasonable inference; - - - - conjecture. (Prepared especially for this edition by Professor W. E. S. Turner, of the Society of Glass Technology, Sheffield, England, and reproduced with his permission.)

eminence in glass passed to Bohemia, Silesia, Germany, France (St. Gobain works), and England. In the latter country there were already 88 glass factories in 1696. Even before that date, in 1675, George Ravenscroft of London produced a new glass, which he called flint glass, and which contained lead oxide, matching in quality and beauty the Venetian "Crystal Glass," which until then had been unequalled. The Bohemian and most other glasses had been soda-lime-silica glasses.

The Glass Industry in the United States. In our Colonial period some early attempts at the establishment of a glass industry are recorded. One which was successful over a period of 11 years was the operation of a glass works at Mannheim, Pennsylvania by William Henry Stiegel, which produced plain, colored, enameled and engraved ware (1763-1774). Soon after the establishment of the United States, a successful works which used coal-fired furnaces was erected at Pittsburgh (1796, Craig and O'Hara) and soon thereafter a number of works were set up in the Ohio Valley. The Boston and Sandwich Company, established in 1826, introduced pressing methods for tumblers, dishes and other pieces. The plant was closed in 1888, when glass making was transferred from New England and New York to the Mid-West under economic compulsion. In the same year William Libbey closed his New England Glass Works and erected a new plant at Toledo, Ohio. Twenty years earlier Amory Houghton had transferred his glass factory from Brooklyn to Corning. The areas which are today still important in the glass industry are southwestern New York, Ohio, Pennsylvania, West Virginia and Illinois. The abundance of natural gas in the Southwest has induced the development of glass manufacture in that region. In addition, the demands of the Pacific coast have encouraged the construction of glass factories there.

The following inventions are selected and listed to exhibit the improvements in the building and operation of glass furnaces and in the manipulation of glass; first regeneratively-fired pot furnace, 1879, Pittsburgh; pressing a bottle parison and blowing it up mechanically, Arbogast, Pittsburgh (1882); first commercially used bottle-blowing machine, Frank O'Neill, 1893; wire-imbedded glass, Frank Schuman, at Tacony, Pa., 1892; mechanically-drawn and blown large cylinders for window glass,[1] American Window Glass Company, Lubbers, 1903; a completely automatic bottle-blowing machine, M. J. Owens, 1905; machine for making glass tubing continuously, E. Danner, 1917; method of drawing flat glass continuously, I. W. Colburn, 1918; continuous rolling and continuous grinding and polishing of plate glass, Ford Motor Company, 1923; continuous ribbon machine for electric light bulbs, Corning Glass Company, 1926; steam-blowing process of Slayter and Thomas, applied to glass fiber production, 1931.

The Modern Glass Industry and the Various Kinds of Glass. The bulk of the glass manufactured today is the soda-lime-silica type: structural glass, container glass and electric light bulbs are of this composition, and account for the greater part of its production. Structural glass includes window glass, wire glass, figured-roll glass, plate glass, glass grilles and

[1] Described in the first edition of this book, 1928.

hollow glass blocks. Container glass includes glass for bottles or other containers for milk, soft drinks, beer, wine, medicines, chemicals and many other products.

Soda-lime glass is made by heating together soda ash, limestone or burned lime, sodium sulfate, some charcoal or other form of carbon, sand, cullet (broken glass), and other materials minor in amount but not in effect. The heating is performed very generally in a large trough-shaped furnace, called the tank furnace. The molten glass from the furnace serves to make any one of the objects and products which have been named. After leaving the furnace it is allowed to cool under controlled conditions, and finally forms the transparent solid glass, which may be considered essentially a mutual solution of silicates possessing so great a viscosity that it behaves, for ordinary purposes, like a solid.

Although silica forms the chief acidic constituent of most commercial glasses, other oxides may partially or wholly displace silica from the glass-forming rôle. Phosphate and borate glasses may be mentioned in this regard. They have special uses; e.g., a phosphate glass which resists hydrofluoric acid vapors was developed for sight glasses in connection with the handling of uranium hexafluoride, in the separation of uranium isotopes during the Manhattan Project.

In connection with silicate glasses, there will be constant reference to three pieces of equipment: a furnace for melting the glass; mechanical devices, which may be very simple or extremely complicated, for shaping the glass while it is plastic, and the lehr, a cooling-off space, in which strains due to uneven cooling are equalized. This last operation is called annealing.

An amount of glass much smaller in tonnage than soda-lime glass is made for optical purposes. Optical glasses differ widely in composition, and are generally referred to as crown or flint glasses,[2] the former containing lime and the latter lead oxide as the chief stabilizing ingredient. These glasses are melted in clay pots, with or without a hood; a single pot is generally fired, but sometimes a number of them are set in a common furnace.

Many other descriptive terms are used to classify optical glasses chemically, as for example zinc crowns, phosphate crowns, fluor crowns, barium crowns, borosilicate crowns, barium flints, and others. In addition, a physical grouping based on density or refractive index is used. Thus, a light flint refers to a lead glass with a lower density and hence a lower index of refraction than a medium or dense flint glass.

The various types of optical glasses are illustrated in Figure 71 in which are correlated the important optical properties or refractive index, N, with the V-value of the glass. The latter value,

$$V=\frac{N_D-1}{N_F-N_C}$$

expresses the effective-refractivity of the glass in terms of the mean dispersion. A glass with a V-value of 55 and over is classed as a crown glass;

[2] The term "crown glass" originated from the fact that the lime glass which was used for hand-blown windows had the shape of a king's crown in one of its stages of manufacture. The term "flint glass," which refers to a lead oxide glass, originated from the common use of flint as a source of silica in these glasses.

one with a V-value below 55, as a flint glass. The relations shown in Figure 71 are important in the design of optical instruments and the production of achromatic combinations.

G. W. Morey [3] has developed wholly new types of optical glasses possessing high refractive indices and unusual relationships between the refractive index and V-value of the glass. The latter important discovery permits the development of "fast" achromatic lens combinations of large

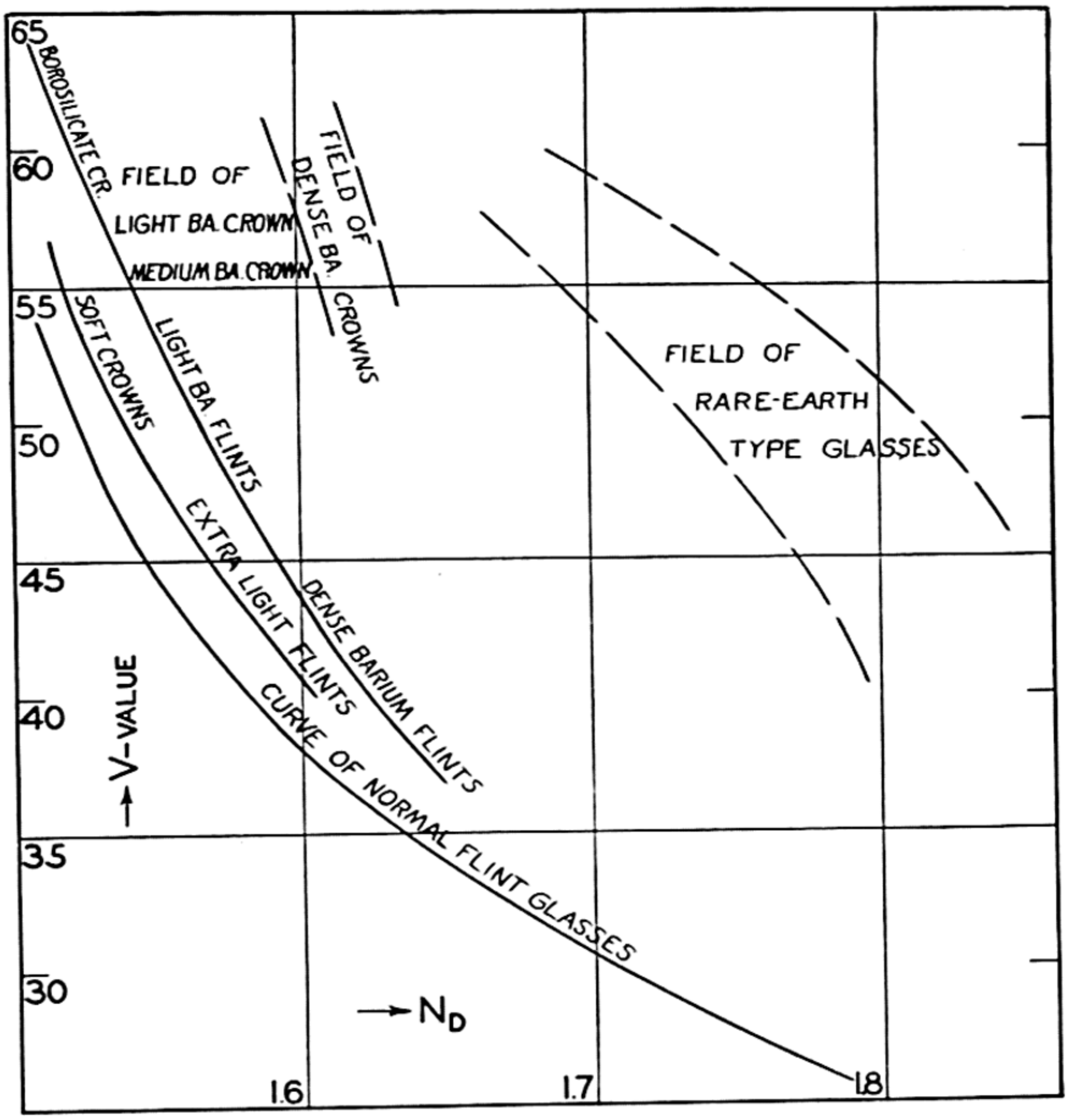


FIGURE 71.—Relation between optical constants of various types of optical glasses.

relative aperture. These new glasses contain oxides which have not been used heretofore as chief constituents in glasses: lanthanum, tantalum and titanium oxides, in combination with boric oxide.

A somewhat different "flint" glass finds usage in cut-glass ware, which calls for a brilliant and colorless glass. It is a potash-lead oxide-silica glass. The lead oxide contributes brilliance by its high index of refraction; potassium oxide produces a glass which may be decolorized by manganese dioxide more completely than a sodium oxide glass. The potash-lead oxide glass is adapted to electrical seals, for its electrical conductivity is lower than that of the corresponding soda-lime glass. Lead glass in the form of tubing is

[3] U. S. Patent 2,150,694 and Reissue 21,175 (1939) to G. W. Morey.

used in making neon signs (which see) because its longer working range facilitates hand-working operations.

Heat-absorbing glass, heat-resisting glass, glass for chemical laboratory ware, x-ray absorbing glass, and many others, some of which will be discussed later, belong to the large group of Special Glasses.

Chemical Composition of Glass. An infinite number of compositions may exist in the glassy state; even a simple three-component system like

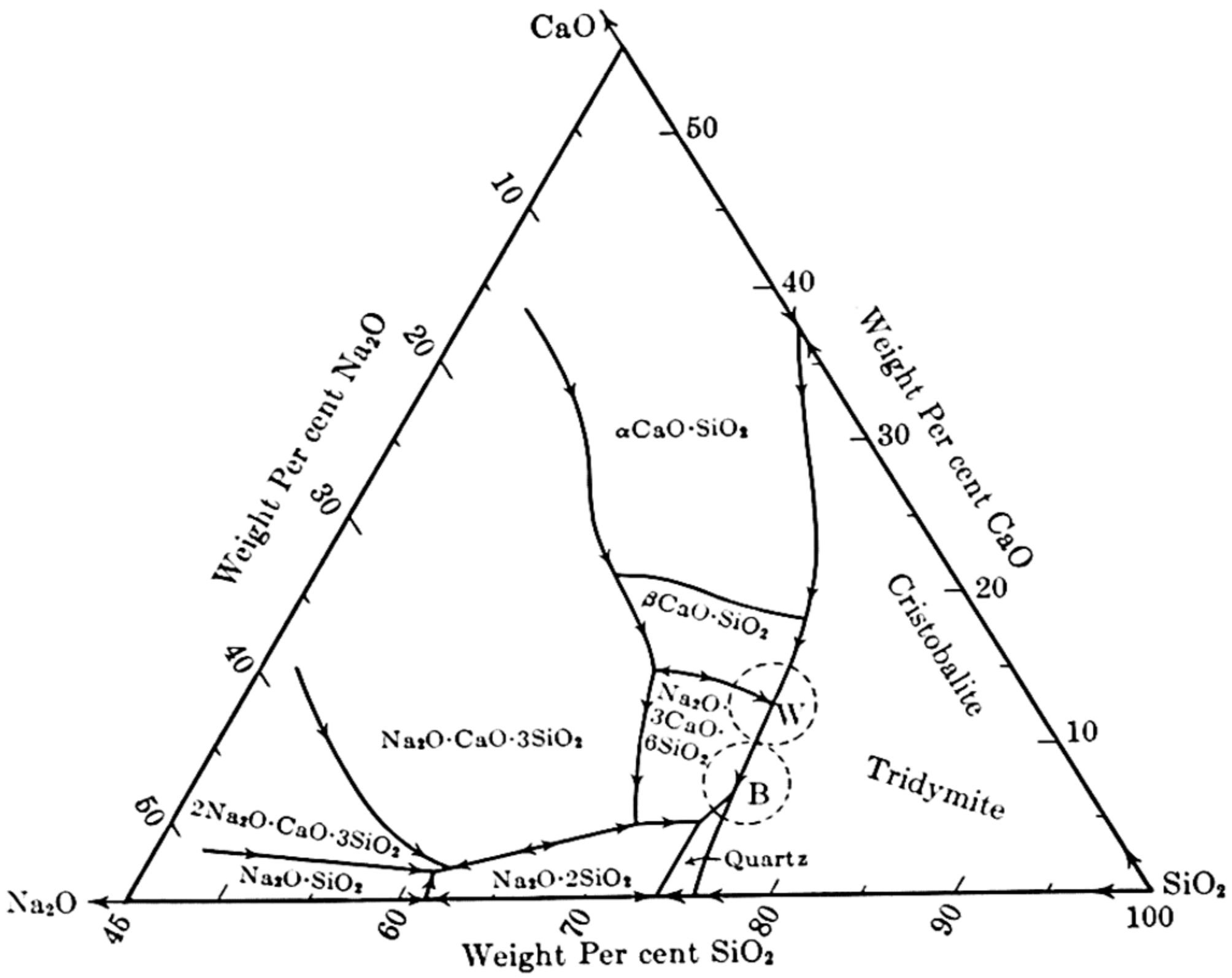


FIGURE 72.—Fused mixtures of soda, lime and silica: Boundary curves limit the areas within which the phase indicated exists. (Courtesy of Donald E. Sharp.)

Na_2O-CaO-SiO_2 has a large composition field in which glasses are formed by rapid cooling (slow cooling would allow some compositions to form crystals, which would destroy transparency). Practically every chemical element may be incorporated in a glass composition, including such noble elements as platinum and gold. Of these many compositions, the two which stand out in commercial importance, and which have already been mentioned, are the soda-lime-silica glasses, and the potash-lead oxide-silica glasses. Although a great variety of compositions of the former glass exists, the field of compositions in commercial use is roughly restricted to that shown in Figure 72 in which bottle compositions are shown within the circle B and sheet glass compositions in the circle W, superposed on a plot of the soda-lime-silica system. It is interesting to observe that the compositions used today for bottle and sheet glass are not greatly different from those of

ancient glass; this is because glass compositions which fall far outside of a restricted field have unfavorable properties. Glasses which are higher in alkali will weather and deteriorate, due to the gradual though slow solution of the alkali in water; those which are higher in calcium oxide are prone to devitrify during manipulations, while glasses higher in silica are too viscous to permit melting and working.

The bottle composition field shown in Figure 72 has been drifting toward the window-glass field during the last decade. The composition of the average bottle glass made in 1946 is given in percentages by Moore and Lyle [4] as: SiO_2 72.1; R_2O_3 1.8; RO 10.1; R_2O 15.6; B_2O_3, SO_3 and F 0.5. The symbol R stands for a trivalent, divalent, or monovalent metal, as indicated by the formula.

During 1947 a soda-ash shortage encouraged the use of smaller amounts of alkali in glass, with R_2O ranging from about 13-14 per cent and RO from 11-12 per cent, SiO_2 being about 73 per cent. Such a composition is within the field of window and plate-glass compositions and the distinction between bottle and sheet-glass compositions may disappear in the future.

TABLE 36.—*Analyses of feldspar, syenite, nepheline and aplite.**

	Feldspar					
	Potash Spar	Soda Spar	Typical No. 17 Spar	Nepheline Syenite Grade A	Nepheline (New England)	Aplite Piney River, Va.
SiO_2	67.93%	68.53 %	69.0 %	60.22%	54.40%	60.34%
Al_2O_3	18.20	19.59	17.4	23.72	26.01	23.76
Fe_2O_3	0.07	0.064	0.08	0.06	0.08	0.31
CaO	0.20	0.71	0.1	0.42	0.95	6.08
MgO	nil	trace	nil	0.09	—	
Na_2O	2.70	9.52	3.0	10.06	12.85	
K_2O	10.50	1.29	10.0	5.04	2.97	
Alkali						8.98
Loss on ignition	0.40	0.28	0.4	0.47	1.50	0.53

* From "Recent trends in glass composition," Donald E. Sharp, *Glass Industry*, (April, 1940).

The three main raw materials for soda-lime-silica glass are now soda ash, limestone and sand. Saltcake (Na_2SO_4) formerly was a cheaper source of sodium oxide, and in years gone by it was used in substantial quantity in place of soda. Today, most of the alkali is obtained from soda ash. It was found, however, that a small quantity of saltcake with the soda was beneficial, so it is now an accepted minor ingredient in the batch formula (see later). Feldspar has generally been used in substantial percentages as an ingredient of opal and alabaster glass. About 25 years ago its use in minor amounts in container glass for improving chemical durability and reducing the tendency toward devitrification began; during the last decade, a uniform and high-quality feldspar has become almost a standard ingredient of container glass. Syenite and nepheline syenite, among other oxides, are ingredients which contribute amounts of Al_2O_3 ranging from 2.0 to 3.5 per cent, to container glass. Still another similar material is aplite, which has been successfully incorporated into the batch formula in spite of its relatively high iron content (Table 36).

[4] "Container Glass Compositions: 1932-1946," by H. Moore and A. K. Lyle; *Glass Industry*, 28, 563 (1947).

Batch formulas for some container glass are given in Table 37.

TABLE 37.—*Batch formulas for machine-blown container glass.*

(Parts by weight)

	"Coca Cola" green container glass	Emerald green container glass	Amber container glass
	1000 pounds	1000 pounds	1000 pounds
Sand	370	370	370
Soda ash	250	250	250
Dol. limestone	100	100	100
Feldspar	15	15	15
Borax	4	4	—
Salt cake	1	1	—
Arsenic trioxide	3 to 5	3 to 5	—
Iron oxide	2 to 4 oz.	4 to 5 lbs	—
Sod. bichromate	1 to 2 oz.	½ oz.	—
Powder blue	—	—	4 to 6 lbs
Iron sulfide	—	—	3 to 4 lbs
Carbon or coal			

The three glass batches of Table 37 form a glass with the following approximate composition, neglecting coloring materials:

SiO_2	73.0%
Al_2O_3	1.3
Fe_2O_3	0.3
B_2O_3	0.4
CaO	5.2
MgO	3.7
Na_2O	15.6
K_2O	0.3
SO_3	0.2
	100.0%

The additional coloring agents are as follows: In the "Coca Cola" green glass, 0.006% Cr_2O_3 + 0.003% CoO; in the emerald glass, 0.15% Cr_2O_3 + 0.001% CoO; in the amber glass, about 0.3% FeS is present instead of the 0.3% Fe_2O_3 listed.

Batch Melting Reactions. After the raw materials forming the batch have been placed in the furnace, chemical reactions take place which finally convert them into a mutual solution of silicates, borates, and other chemical compounds, accompanied by the evolution of large quantities of gas (about 12 cu ft of gas at furnace temperature for each pound of glass). The gas evolved performs the important function of stirring and homogenizing the "melt," as the batch is called. Figure 73 summarizes the reactions which were found to occur in a finely powdered sodium carbonate-calcium carbonate-silica batch, and Figure 74 those in the more complex system in which sodium sulfate replaces sodium carbonate. The reactions in the tank furnace are of the same general nature, but are modified by the presence of minor amounts of materials which are added to the batch to promote melting and fining or to improve the properties of the finished ware. It should be pointed out that a number of reactions take place simultaneously.

At the end of the reactions, most of the gases have escaped and the melt enters the stage of "open boil," when small bubbles or "seeds" rise through

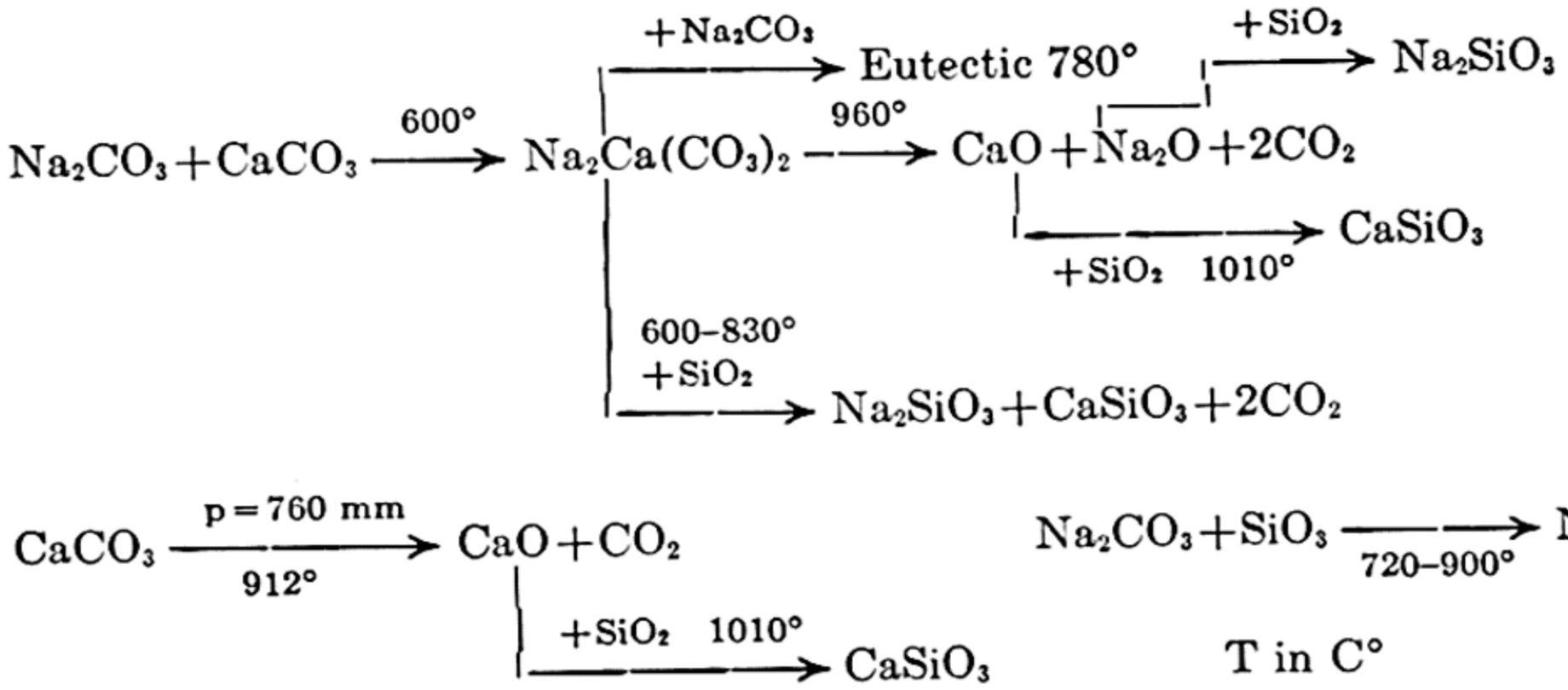


FIGURE 73.—Some melting reactions in the batch: 1000 SiO_2+400 $CaCO_3$+300 Na_2CO_3 (*After Tammann and Oelsen*).

the melt; gradually the melt becomes "fine," that is, free of bubbles. Some of the chemical reactions in the furnace are slow even at high temperatures (as $Na_2SO_4+SiO_2$); therefore a glass melt may require considerable time to reach a state of equilibrium.

Technical and Chemical Glassware. Window glass is used because it admits light into buildings while keeping out the weather, and because it is cheap. Optical glass is used to refract, disperse, or condense light. Heat-resisting glass owes much of its economic value to its low coefficient of ex-

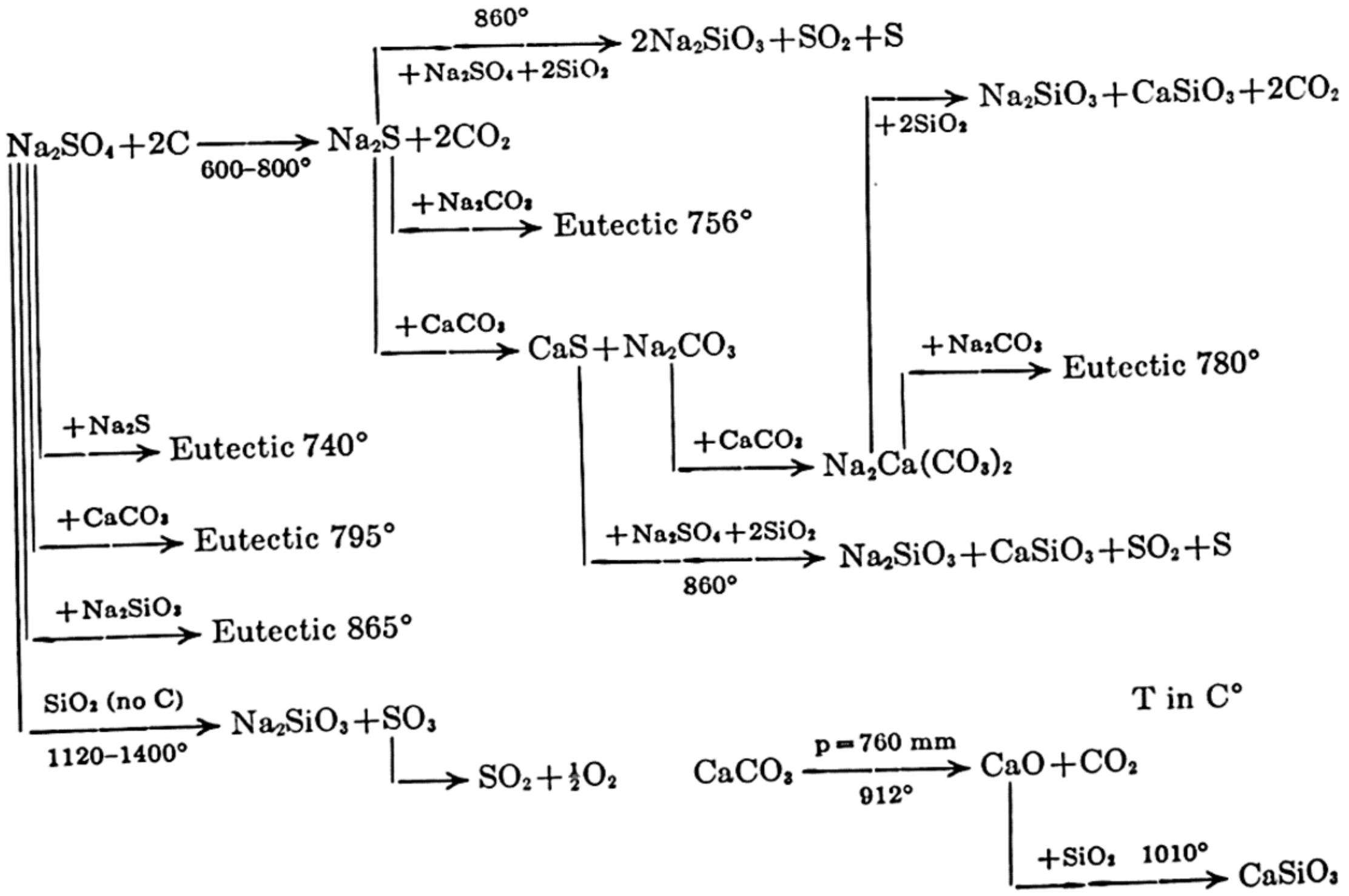


FIGURE 74.—Some melting reactions in the batch: 1000 SiO_2+400 $CaCO_3$+400 Na_2SO_4 +25 Carbon (*After Tammann and Oelsen*).

pansion: it can be heated rapidly, or cooled suddenly and unevenly without breaking. The best known of such glasses is "Pyrex" Brand which is made into baking dishes, teapots and laboratory glassware. The breakage of "Pyrex" Brand beakers and flasks is so low and its resistance to chemical reagents so high that it has been universally endorsed, although it is somewhat higher-priced than common glassware. Before the War of 1914-18 Jena glass, also remarkably heat- and shock-resisting, was largely used in the United States. Typical formulas for Jena glass and for "Pyrex" Brand chemical ware are given below:

	SiO_2	B_2O_3	Na_2O	Al_2O_3	As_2O_3	K_2O	MgO	CaO	Fe_2O_3	ZnO
	(In per cent)									
"Pyrex" Brand	80.62	11.90	3.83	2.00	0.66	0.61	0.29	0.22	0.12	
Jena	64.58	10.03	7.38	6.28	...	...	0.12	0.08	0.10	11.78

"Vycor." A new form of low-expansion glass consisting essentially of silica has been developed and is marketed under the general name of "Vycor" by the Corning Glass Company. A borosilicate glass of special composition is made into the ware and then heat-treated, whereby it is caused to separate into two phases. It is opalescent at this stage. By means of mineral acids, one phase, consisting essentially of a borate complex and comprising about 36 per cent of the glass, is dissolved, leaving a translucent body containing a multiplicity of pores. On further heat-treating, the pores are closed while the ware shrinks about 20 per cent, and there results a transparent product consisting of 96 per cent silica, highly resistant to thermal shock.[5]

Colored Glasses. Since colored glasses are generally made in comparatively small amounts, clay pots are often used for melting the batch. The clay pot of usual dimensions holds 1000 to 2000 pounds of glass. There are four principal methods for producing color in glass: [6] (1) by dissolving in the glass a colored ion of a transition element,[7] for example, cobalt; (2) by forming colored crystals in the glass or glaze, *e.g.*, red chrome glaze; (3) by dispersing a colloid throughout a transparent glass, such as colloidal gold in gold ruby glass; (4) by developing a chromophore in which two elements share, for example, Se-CdS (selenium red). The products belonging in the first class are not influenced by reheating, but those in the other three are. It should be noted also that the kind of glass to which the method is applied has a bearing on the result.

The manufacture of red automobile tail lights will serve as an example. A batch for the red glass is placed in a closed pot (Figure 75) which stands within the furnace. The batch composition may contain, for instance, soda and zinc oxide with 1 per cent of selenium and 1 per cent of cadmium as

[5] "Shrunk glass resists extreme heat and cold," *Glass Industry*, 20, 269 (1939); U. S. Patent 2,106,744, Canadian Patent 364,157, British Patent 442,526, to H. P. Hood and M. E. Nordberg. Also "Recent trends in glass composition," by Donald E. Sharp, *Glass Industry* (April, 1940).

[6] "Color formation in glasses and glazes," F. H. Norton, *Glass Industry* (February, 1935).

[7] The transition elements have an incomplete shell of electrons in proximity to the valence electrons. Color is associated with the light (energy) emitted when an electron slips from a high energy level to a lower energy level. Among the transition elements are V,Cr,Mn,Fe,Co,Ni,Cu,Au.

cadmium sulfide. After the materials have melted and the glass melt is ready, the pot is worked by two men and one boy. One man gathers gobs of clear glass from the inner ring in the pot on his "punty," and drops them, one at a time, into a mold, disconnecting the gob from the gathering tool by means of shears. The second man operates the die which, with the mold, forms the finished shape. The boy places the shapes on a flat tool and carries them to the lehr. The percentage composition of one such red glass is as follows: SiO_2 71.3, ZnO 10, Na_2O 11.5, K_2O 4.5, B_2O_3 0.3, cadmium as CdO 1.4, Se 1.

Ruby red may be produced by adding cuprous oxide to a potash-lead glass. On cooling, the glass is practically clear, and the splendid red color

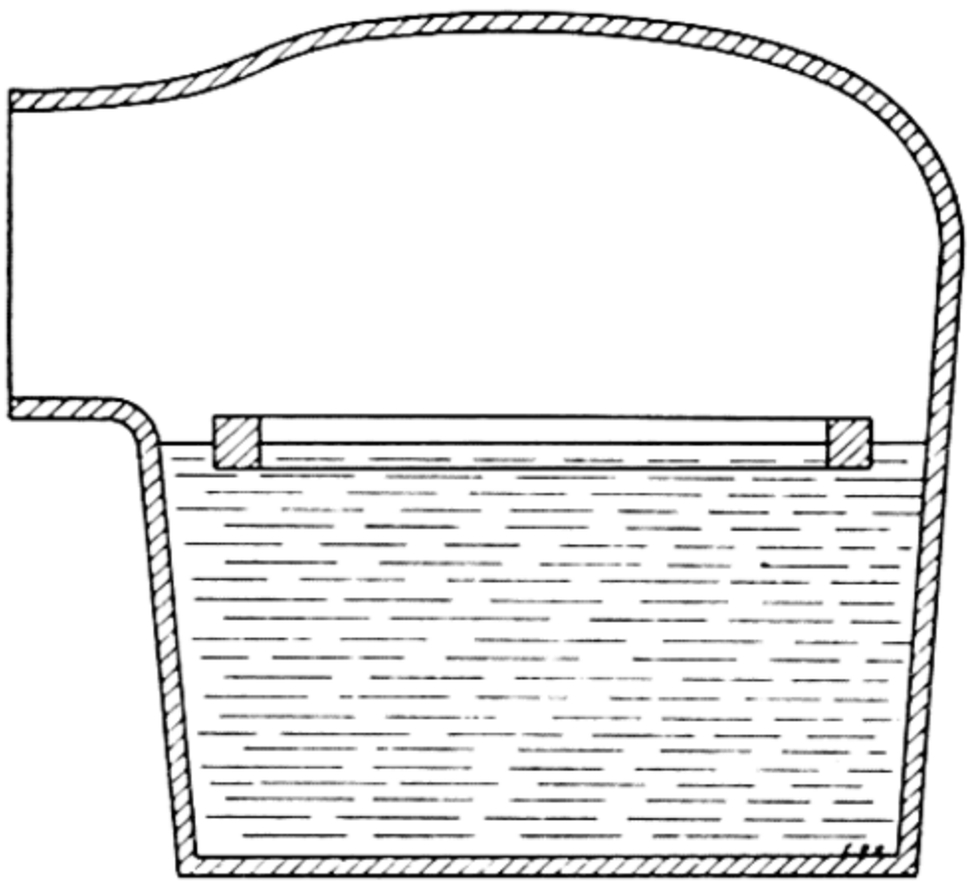


FIGURE 75.—Closed pot used for small lots of glass of window-glass grade and for colored glass. A clay ring floats on the glass; within the ring, the surface of the glass melt is kept clear.

develops after reheating. Gold ruby is made by adding gold chloride to potash-lead glass; after working, the glass is reheated to develop the wine-red color. These two glasses belong to class (2); in fact, it was in the study of gold ruby glass that Zsigmondy made the observations which have led to much of the present important knowledge of the colloidal state of matter. The color is due to highly dispersed, but discrete, particles of gold, visible in the ultramicroscope.

Yellow glass may be made by adding cadmium or uranium oxide to soda-lime glass; or by adding 2 per cent of cerium oxide and 2 per cent of titanium oxide to the same kind of glass, producing a brilliant light yellow.

The deep blue color of cobalt is obtained by adding cobalt oxide to soda-lime glass. A greenish-blue is made by using cupric oxide. Amber glass results from the admixture of a carbonaceous material with sulfur or iron sulfide in a soda-lime batch. Green glass owes its color to chromium oxide or sodium dichromate addition. Black glass can be made by using an excessive amount of pyrolusite and iron oxide.

Nearly all commercial glass has a trace of color. *Tank glass* is *decolorized* by addition of selenium. Only potash-lead glass is decolorized by means of the once universally used decolorizer, manganese dioxide.

Colored glass absorbs the visible wave lengths; *heat-absorbing glass* absorbs the long waves in the invisible. In nearly all compositions for the

latter glass, the ferrous ion is the constituent which is the active absorber. The ferrous ion is chosen because of its strong absorption in the infrared region.

Opal Glass. Opal glass is made by substituting a combination of calcium fluoride and feldspar for part of the ingredients ordinarily used in making soda-lime glass. Other fluorine- and alumina-containing materials, such as sodium silico-fluoride, cryolite and nepheline syenite, may be used in place of fluorspar and feldspar. A typical "heavy" opal glass might have the percentage composition: SiO_2 68-69,Al_2O_3 3-4;CaO 4-6;ZnO 2-3;Na_2O 15-16;F_2 3-4;minor oxides 1-2.

Opal glasses are opaque; they diffuse light by virtue of countless tiny inclusions called crystallites which differ in refractive indices from the surrounding glass, and therefore reflect and refract the light.[8] The crystallites in this glass are a mixture of sodium fluoride and calcium fluoride. While the glass is melted, it is limpid; it becomes opaque on cooling; this is called the "striking" of the glass.

Light globes of all kinds, for internal lighting fixtures as well as for street lighting, are made of opal glass. It has smooth surfaces easy to keep clean, and also has illuminating advantages over frosted glass or other glass which diffuses by virtue of irregularities in its surfaces.

Cosmetic and ointment jars are among the products made of opal.

The term "alabaster glass" refers to glass which appears white when thin sections are viewed by transmitted light, whereas opal glass has a fiery tinge under these conditions.

Modern Machine Development

The development of modern glass-making machinery may be said to have started in 1825, when a simple hand-operated piece of equipment, the side-lever press, was introduced. A workman gathered some glass on a punty and dropped it into a cavity which is now designated as the mold; a plunger then forced the glass to fill all parts of the mold to form the article. (Compare selenium red glass.) From this simple equipment the intricate and elaborate machines, which now produce bottles by the million each day, have been developed step by step. The earlier "blown" articles were inflated by human lung power, against the sides of the mold; when the machine blow was introduced, variations in the blow were eliminated, and better control of raw materials and of temperature became imperative. Improvements in the methods for making window glass came more slowly. First the hand-blown cylinder—really no more than a large bottle with top and bottom cut off, then opened lengthwise and laid in the heat to flatten—was imitated by machine-blown cylinders. Then came the flat glass drawing machine, fully automatic, by which all the window glass in the United States is now made. Plate glass resisted longest, but has succumbed finally to mechanical methods, including continuous grinding and polishing of its surfaces.

(1) Window Glass. (*a*) *Hand-blown cylinders.* The method of mak-

[8] "Diffusing glasses for illumination," Henry H. Blau, *Ind. Eng. Chem.*, 25, 848 (1933).

ing flat glass from hand-blown cylinders has survived in certain glass houses devoted to special products,[9] such as lights for stained-glass church windows, opal glass sheets, and colored glass for various applications. The gatherer inserts the blow pipe (1″ O.D., ¼″ I.D.) into the pot and collects at the end of the pipe a "gather" of glass from the melt. After cooling the pipe in a spray of water, he rests the ball of glass on a shaped piece of oak and slowly turns it while gently blowing, in order to give it its initial shape. At the right moment, a helper directs a stream of compressed air onto the neck of the cylinder, chilling it and thus fixing the size. The load of glass, or "parison," is reheated and blown with caution while being held over the pit next to the "glory hole." After blowing and reheating, it is swung gently in the pit, with a pendulum-like motion, until it elongates to the desired

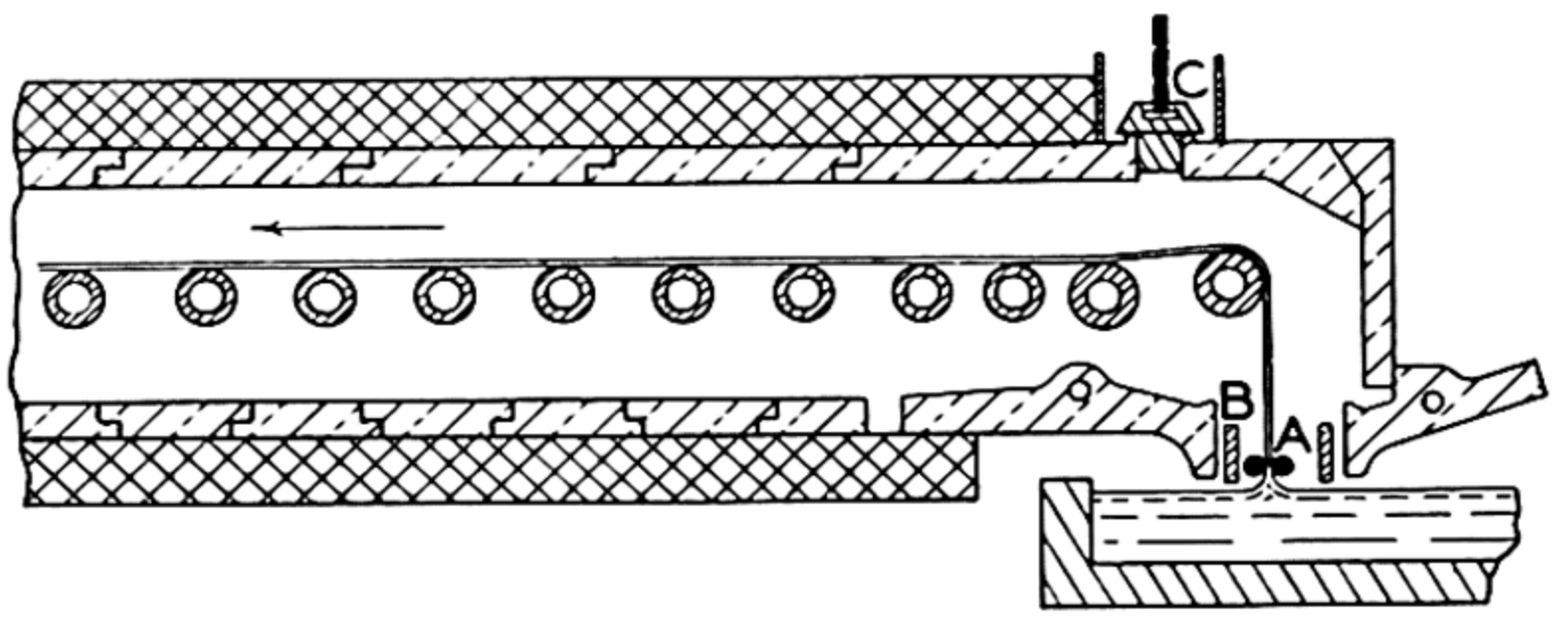


FIGURE 76.—The Libbey-Owens-Ford flat glass process, the bending roll or Colburn process. A, the knurled rolls which maintain the width of the sheet; B, sheet coolers with water circulation; C, adjustable closure block for the regulation of temperature.

length by its own weight aided by blowing. Reheating of the thicker portions in order to blow them thinner is frequent. The operation requires practice and skill. The completed cylinder is carried to a stand and enough glass removed from the two ends to leave an almost perfect cylinder. Cutting is done by a string of glass taken from the furnace and wound around the cylinder; it is then quickly removed and the heated portion touched with a cold rod, whereupon the end pieces fall away neatly. The cylinder is slit lengthwise by running a hot iron inside the glass and then touching the hot line with a wet rod. After applying wooden clips to the edges of the new cut, the cylinder is carried to the flattening furnace where it opens, aided by the touch from a wooden tool, and finally flattens. The flattened sheet is carried to a lehr for annealing. The maximum size of the sheet is about 4 feet by 3 feet.

(*b*) *Colburn Process.* In the Colburn process,[10] a flat sheet of glass, often referred to as a ribbon, is drawn vertically from the glass melt in the furnace,

[9] Such as the L. J. Houze Convex Glass Company, Point Marion, Pennsylvania, described in "Pittsburgh People" (*Pittsburg Plate Glass Employees*), May, 1946.

[10] Irving W. Colburn, whose process, with numerous improvements, is now used by the Libbey-Owens-Ford Glass Co., Toledo, Ohio. Some of the improvements may be studied in U. S. Patent 2,267,604, to J. L. Drake. The plants are located at Shreveport, La., and Charleston, W. Va.

passes over a bending roll and continues its travel in a horizontal direction (See Figure 76). Each machine works in a drawing pot, which is an extension of the tank furnace; there are usually two drawing pots for each furnace. As the sheet leaves the melt, it tends to contract in width and requires support: two sets of water-cooled, knurled rolls engage the sheet for a distance of about 2 inches, thus maintaining a predetermined width of about 100 inches, at the same time thickening the edges. Water-cooled shields protect the newly formed sheet from the excessive heat of the funace; the glass sheet, however, is still in the plastic state, maintained partly with the aid of gas burners. The plastic sheet reaches the bending roll, is turned

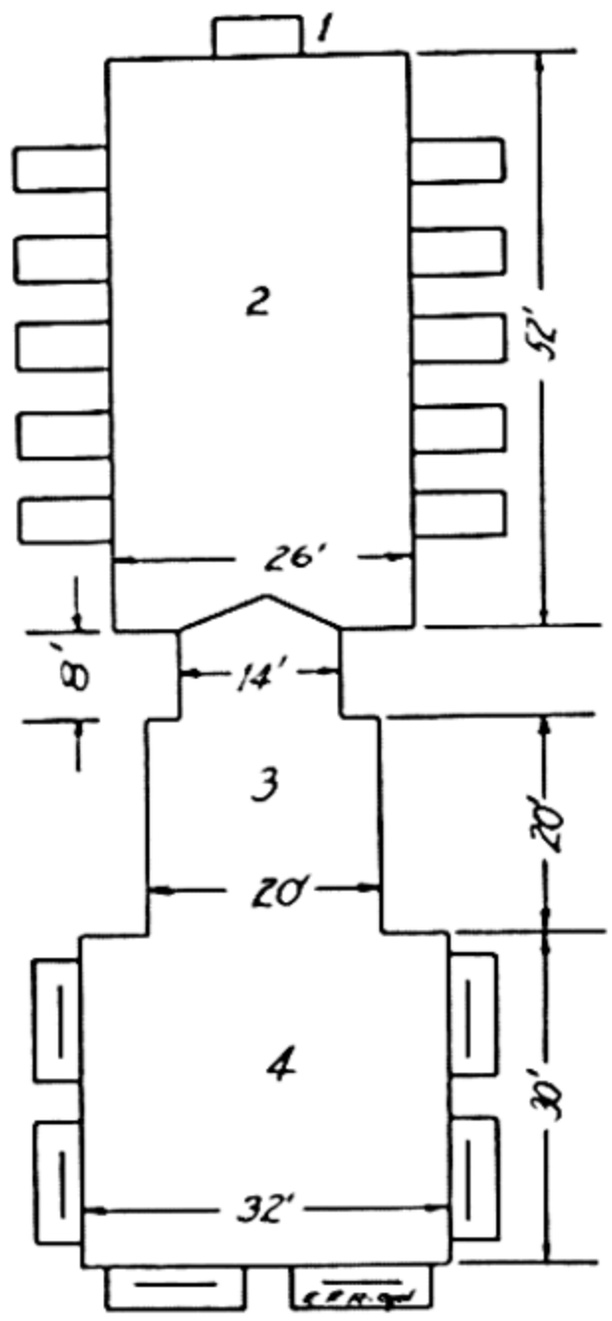


FIGURE 76a.—Plan of furnace for window glass by the Fourcault machines. 1, the dog house, or charging trough; 2, melting end; 3, refining end, with neck between 2 and 3; 4, drawing chamber, surrounded by the work pits, each one with its drawing machine. Between the melting end and the neck are the floaters. Five inlets or "ports" on each side of melting end for combustion air are shown.

through an angle of 90°, and now travels horizontally through the lehr, in which 200 asbestos-covered power-driven rolls keep it moving at the right speed to the movable cutting table. On the latter the continuous sheet is cut into suitable sizes; these are put through a continuous washing machine and then distributed to the cutting stalls. The sheets are graded (by blemishes per unit area), cut into commercial sizes and packed in boxes each containing 50 square feet of glass. The sheet glass made by this process is flat and free from major distortion.

(c) *Fourcault Process.* The Fourcault process produces flat glass for windows mainly, but also for doors, cupboards, closets, show cases and the like. More than a third of the window glass produced in the United States is Fourcault glass. The sheet is drawn vertically upward, and continues upward through a short lehr to the cutting floor. The essential feature of the Fourcault process is a long rectangular clay piece, with a longitudinal slot, through which the glass is "paid out"; hence the term *débiteuse*. Each drawing machine occupies a work pit, and several work pits are grouped

around the refining end of the tank furnace. These arrangements will be clearer from a description of the tank furnace and its operation which follows, after which some further remarks on the Fourcault process will be offered.

The *tank furnace* is of the continuous type, with continuous feed, or batch feed at regular intervals, and continuous draw; it is run without interruption until the refractory walls give out. It is fired by gas, for example, natural gas. The combustion air is preheated by passing it through the regenerators located at the side and below the furnace. The plan for such a tank furnace 102 feet in overall length is shown in Figure 76a. It is built of three kinds of bricks and forms: (1) Silica bricks for the roof

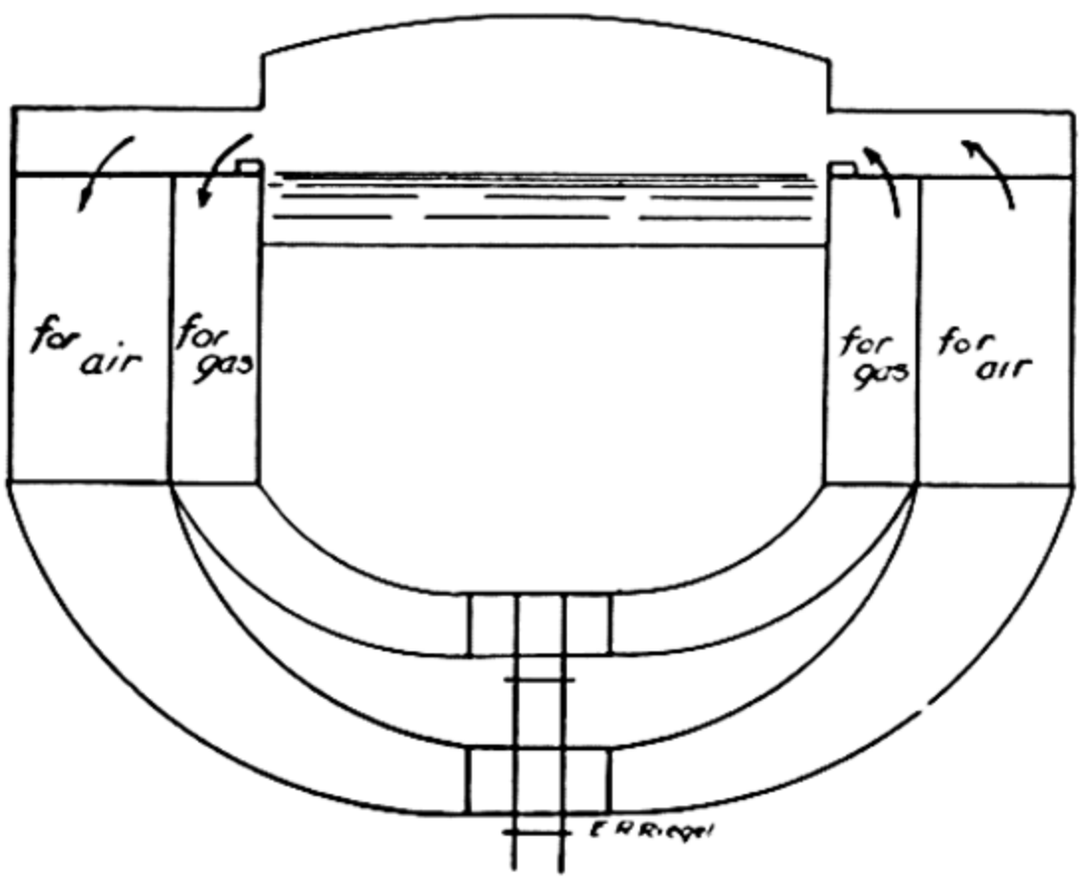


FIGURE 77.—The regenerative chambers shown as they would be constructed for producer gas firing. As shown in the sketch, the chambers at the right are giving up their heat; those at the left are storing heat. The chambers are filled with a checker-work of brick.

or arch, commonly called the cap; (2) refractory blocks for those upright walls which do not come into contact with the molten glass; and (3) "flux" blocks, of a special composition of fireclays, which resist glass attack, and which are employed for those walls which do come into contact with the molten glass and must contain it. A fourth kind of brick and shaped slab is being used more and more in the construction of glass furnaces, below the glass line, namely, *Corhart blocks*, manufactured by electrical melting of a composition equivalent to that of mullite, and cast in suitable molds. Corhart blocks have a very dense structure and are extremely resistant to the corrosive action of molten glass. A new Corhart fused block with high content of zirconia has recently been introduced under the trade mark of "Zac."

After its construction, the furnace is heated gradually, undergoing expansion during this heating. To accommodate this expansion, the roofing arch rests on skew-backs which are carried by horizontal steel beams integral with steel uprights. The distance between the latter (across the furnace) is adjustable.

Gas and air meet just inside the furnace, so that the flame forms at that point and sweeps across the width of the furnace, passing out through the regenerators on the other side (north side, for example), which now are

brought to a high temperature. After 20 minutes, the direction of the gas and air is reversed; they are admitted at the north side, sweep across the furnace and now heat the regenerators at the south side. The reversing is done by hand.

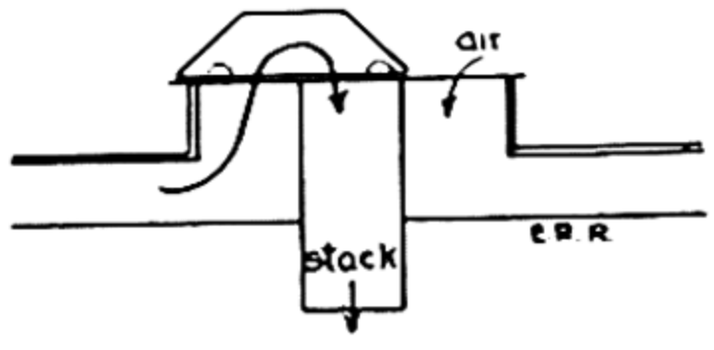


FIGURE 78.—The device for reversing the direction of the flame. A box with open bottom is set as shown, when chambers at the left in Figure 77 are storing heat. After 20 minutes, it is moved to the right, and the inlet for air is then the left passage.

The materials for making the glass are fed in at the "*dog house*," at 20-minute periods. A batch consists of about 1800 pounds of mixed raw materials and 1000 pounds of cullet. A typical batch is given in Table 38.

TABLE 38.—*Batch formula for soda-lime glass, Fourcault process.*

Sand	1000 lbs.
Soda ash	285
Dolomite limestone	285
Calcite limestone	50
Salt cake	90
Feldspar	90
Carbon	2
Cullet	1000

When the batch is melted, volatile materials (such as CO_2 and SO_2) pass up the stack with the flue gases. There is also a slight loss of alkali and lime by volatilization or dusting, and an increase in silica and alumina from the refractories, which are slowly dissolved. The actual glass analysis therefore always differs significantly from the analysis calculated from the batch. For every 100 lbs of the batch just listed, without cullet, about 81.5 lbs of glass would be drawn from the furnace; with the cullet addition as shown, about 88 lbs of glass would be produced.

The percentage composition of the glass would be approximately as follows:

SiO_2 . . . 72.3 CaO . . . 7.8 MgO . . . 4.2 Al_2O_3 . . . 1.0 Na_2O . . . 14.7

The materials are dropped from overhead bins into a mixer suspended on scales, carefully weighed and thoroughly mixed. The cullet comes largely from the plant, partly from outside purchase. As the materials enter the furnace, they gradually melt, and evolve gases quietly. As one looks into the furnace, the surface is white for a distance of 6 feet; small pits about 1 inch across may be seen ("*rabbit tracks*"). Further out, there still is white matter, and a pattern not unlike ribbed sea-sand is visible ("*gingerbread*"). A small pool some 6 or 8 inches across, caused by excess salt cake, which the glass man attempts to avoid, is called "*salt water*." One-third of the way down the melting end, glass has formed, and whiteness is no longer visible. Just in front of the floaters, which force the glass to travel beneath them, the operator watches for a faint line of white bubbles, which should

be absent. The chemical reactions in the soda-lime-silica glass batch have been given. (p. 202).

Between reversals of gas and air, the furnace is absolutely quiet for some 30 seconds, and a view may be had of the glass pool, which reflects every detail of the roof and sides; so quiet is the pool that it takes a little study to tell where glass ends and exposed wall begins. It is a beautiful sight; a few seconds later, the flames have appeared and fill the whole space, cutting off the view.

The hottest part of the furnace is roughly half way down the melting end, for example, 2600° F. (1427° C.); at the floater hole, just in front of the floater, the glass itself is 2430° F. (1332° C.). The preheated air is brought to 2200° F. (1204° C.). The gas consumed per day is 800,000 cubic feet for natural gas. The capacity of the furnace is 1200 tons of molten glass, when the level is carried at a certain height, such as 58 inches; one inch represents 22 tons of glass. The work pits draw approximately 60 tons of glass per day.

There is a variation in the operation of different tank furnaces for window glass. In the newer furnaces, the melting temperature has been increased to 2750° F. (1510° C.). The source of heat may be producer gas, and when it is, a double regenerator is constructed. The gas leaves the producer hot and is prevented from cooling by insulation; it reaches the regenerator for gas with a temperature, for example, of 1100° to 1300° F. (600° to 704° C.); the regenerator raises it to 1800° F. (982° C.).

A gradual eating away of the refractories at and below the level of the glass occurs, especially near the "dog house." The customary remedy is to install a set of water-cooled pipes in contact with the outside of the wall blocks at the regions of greatest corrosion, or to use a fan and duct system which blows air on the most sensitive regions. The degree of corrosion is reduced, but even with these aids, blocks sometimes are completely eaten away, until, if water-cooled pipes have been installed, the glass itself is in contact with them, and congeals, forming its own retaining wall at those places. Thanks to this innovation, the life of a furnace has been greatly extended. One run of 45 months is on record; a life of 24 months is now considered satisfactory, whereas formerly, 9 months was a long life.

The glass travels slowly through the neck into the refining end of the furnace, finally reaching the work pits where the drawing machines are situated. The temperature of the glass in the pits is 1860° F. (1016° C.), which is right for the Fourcault procedure. The débiteuse floats on the glass melt, as has been said, and it is forced down a short distance into the glass melt by adjustable arms; its delivery slot is protected by raised edges, so that no glass reaches it from the surface, but a tongue of glass is forced up from below. The sheet is started with an iron bait which is raised through the lehr and then broken off, while the sheet itself is pulled up by asbestos covered rollers which bear against it. As the sheet leaves the débiteuse, it is cooled by two coolers placed as shown in Figure 79. It will be observed that the rollers on the left side are driven; those on the right are

suspended on hinges and free to move outwardly; they bear against the sheet by the weight placed on the outside of the hinge. The lehr is kept warm by a flame so placed that the temperature gradually decreases as the distance from the furnace increases. The sheet reaches the end of the lehr, emerging on the cutting platform, where it is cut into large sheets while in motion. A straight line is made by a steel wheel cutter by pulling it across the glass sheet while resting it on a light wooden frame which the rising sheet lifts with itself. The lehr is 25 feet high, and the time of annealing

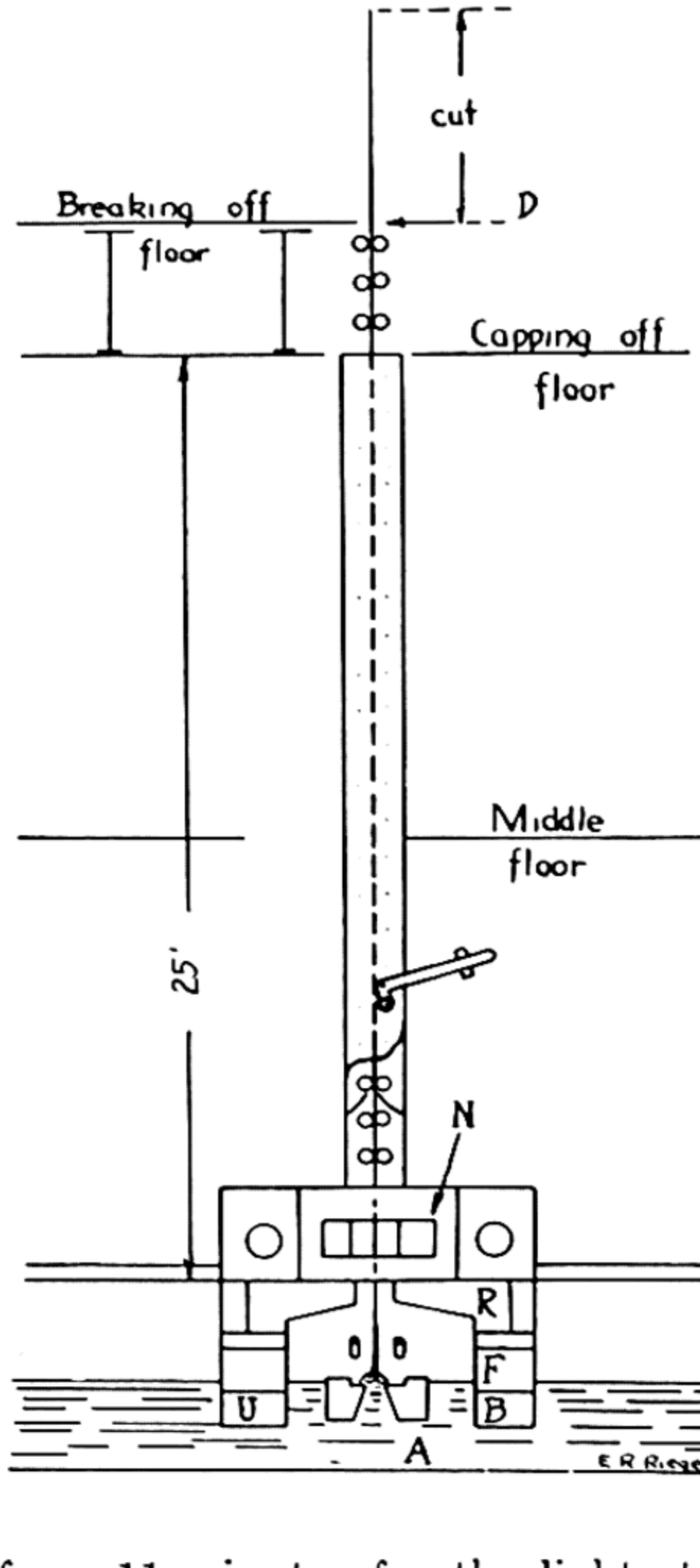


FIGURE 79.—Side elevation of a Fourcault drawing machine. *A*, the débiteuse, clay block with slit; *U* and *B*, underbridge; *F*, bridge; *N*, annealing box with burners; *D*, level at which cutter line is drawn. The sheet coolers are shown just above the débiteuse.

varies with the speed of drawing, from 11 minutes for the lightest glass to 45 minutes for the heaviest. A vane under each of the rollers deflects any broken glass which may drop down the lehr, and ejects it through small swing doors.

The same débiteuse serves for all thicknesses ("strengths") of glass; the strength is controlled by four factors: (1) temperature: the higher it is, the thinner the sheet; (2) depth of block in the melt: the deeper it is, the thicker the sheet; (3) sheet coolers; the closer, the thicker the sheet; (4) the

speed of draw: the higher the speed, the lower the strength. The rates of draw are roughly as follows:

	Inches per minute	Width (inches)	Annealing time (minutes)
For single strength	28	62	12
double strength	18	63	17
heavy strength $\frac{3}{16}$"	11	65	27
heavy strength $\frac{1}{4}$"	7	65	45

(Figures collected some years ago; probably lower than actual draw at this time.)

As the sheet forms, a heavy edge develops and necessitates a recess in the asbestos rolls, as indicated in Figure 80. The edges of the sheet are

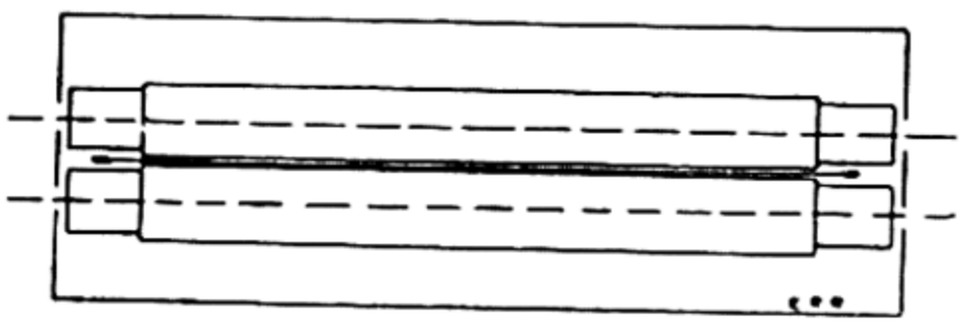


FIGURE 80. — Horizontal cross-section through the Fourcault lehr, showing two asbestos rollers, and the glass sheet with its thickened ends. The rollers are made smaller in diameter at the ends in order to accommodate this extra thickness.

removed on the cutting floor, by trimming 3 or 4 inches off the sides, and are sold for glass shelvings in small medicine closets, show counters and the like. The cut sheets are placed in a warm dilute hydrochloric acid bath for a short time, to remove sublimed alkaline salts which later would cause dullness. From the cutting floor, the cut sheets are wheeled to the cutting room, where the glass is sorted and defects removed, care always being taken to produce useful sizes. The grades are A, B, and C, defined by one of the government agencies. The largest sheet made by this process is 120 inches by 60 inches.

(2) Plate Glass. The composition of plate is approximately the same as that of window glass, and is also soda-lime-silica; it is usually thicker than window glass, for the sake of strength in the finished plate, and also to reduce breakage in the long process of grinding and polishing which it invariably undergoes. The distinguishing feature of plate glass is that it is free of distortions, and that its surfaces are absolutely true. The earlier method consisted of melting the glass in clay pots, lifting a pot by mechanical tongs, and pouring its contents onto a cast-iron table (built in segments), and then leveling by means of a heated roller. The sheet was annealed, set in plaster of paris on a flat table, and ground first with sand, then with emery,[11] and finally polished with rouge, by means of a mechanical grinding head, on one side. The plate was then turned, and the process repeated on the other side.

There are now several modern methods which produce a continuous sheet of glass thick enough for plate glass. In the Pittsburgh Plate Glass Company's method, molten glass from a tank furnace is fed continuously between two water-cooled rolls about 12 inches in diameter; the formed sheet travels through a gas-fired lehr 400 feet long.[12] The Libbey-Owens-Ford Glass

[11] Emery is the natural crystallized alumina (Al_2O_3); rouge is the oxide of iron obtained by roasting copperas ($FeSO_4 \cdot 7H_2O$).

[12] See a two-page diagram for "Plate Glass Manufacture," *Ceramic Industry*, p. 78-79 (July, 1947).

Company's method has two iron forming rolls, 12 inches in diameter and 84 inches long, which revolve toward each other in the molten glass in an extension of the tank furnace itself, and raise a sheet of glass upward for about 2 feet. The sheet is about $\frac{3}{16}$" in thickness, and is drawn upward to a bending roll and thence through a horizontal lehr. The annealed sheet, 80 inches wide, is cut into 10-foot lengths, which are put through the grinding and polishing processes. While in the rough state, the plate glass blanks are handled by means of vacuum cups connected by chain and rod to an overhead crane, with perfect safety to the personnel.

In the Ford continuous sheet process,[13] the glass flows from the furnace onto the metal table, and is leveled by passing under two "Nichrome" cylinders, the second smaller than the first. The glass sheet continues into the lehr, 500 feet long, where it cools from about 1100° F. (593° C.) at the entry to 100° F. (38° C.) at the exit.

Safety Glass. There are two types of safety glass. One is laminated plate glass, which consists of two sheets of plate glass cemented together by a sheet plastic, forming as transparent a whole as the component parts singly. Such laminated glass may be shot through by a bullet without shattering; it breaks and is pierced, but the segments remain in place. Originally a thin sheet of pyroxylin was used; cellulose acetate plastic, and acrylate resin plastics were successive improvements. Of special merit is polyvinyl acetate resin, made by treating polyvinyl alcohol with a moderate amount of formaldehyde, and with softeners and plasticizers. A safety glass containing polyvinyl acetal resin, after being broken, may be rolled into a bundle without shedding the fragments: the resin stretches. There is also in use a polyvinyl butyracetal plastic which will elongate 300 per cent.[14]

The other type of safety glass is tempered plate glass which does not shatter even under severe blows. It is a single sheet of quenched glass, with hard surfaces resulting from the compressive stress existing near the surface.

A *double glazing unit* consists of two plate glass sections held a definite distance apart by a metallic seal at the edges (L-O-F Thermopane). The inner plate is thus insulated from the outer one, and does not condense moisture. The unit is thin enough to give the appearance of being one plate.

Structural and Architectural Glass. An important structural glass aside from window glass and plate glass is wire glass. It is made by laying a steel wire netting into the soft glass between two rolls immediately after the glass has been fed from the furnace (Figure 81). The operation is continuous, and a sheet 5 feet wide can be made at the rate of 20 feet a minute; it is cut by bending it in the shape ⌐|_, when the wire breaks off easily. Figured glass, often called Florentine glass, is made by forming the sheet between two rolls, which have a design cut on one or both. When the design is a square or a cube which must retain the proper shape to give the desired

[13] "Making glass for Ford windshields," F. J. Huntley, *Glass Industry*, 4, p. 1 (1923); "Continuous process for plate glass at Ford River Rouge plant," E. P. Partridge, *Ind. Eng. Chem.*, 21, 1168 (1929).

[14] *Glass Industry*, 20, 450 (1939).

effect, the sheet is formed on a table, and a roll bearing the design passed over it. It is pressed glass on a large scale.

Grilles and other shapes of "Pyrex" Brand are examples of the architectural glass known as Corning-Steuben; vases, bowls, and other table pieces decorated by cutting belong to the artistic products known as Steuben ware.[15]

The *glass construction blocks*, which are in popular demand for small and large windows in buildings of all types, are a form of pressed glass. The block is hollow, and is made of two halves which have been pressed to shape; the hot halves are united by fusion and the inner space thus sealed. After

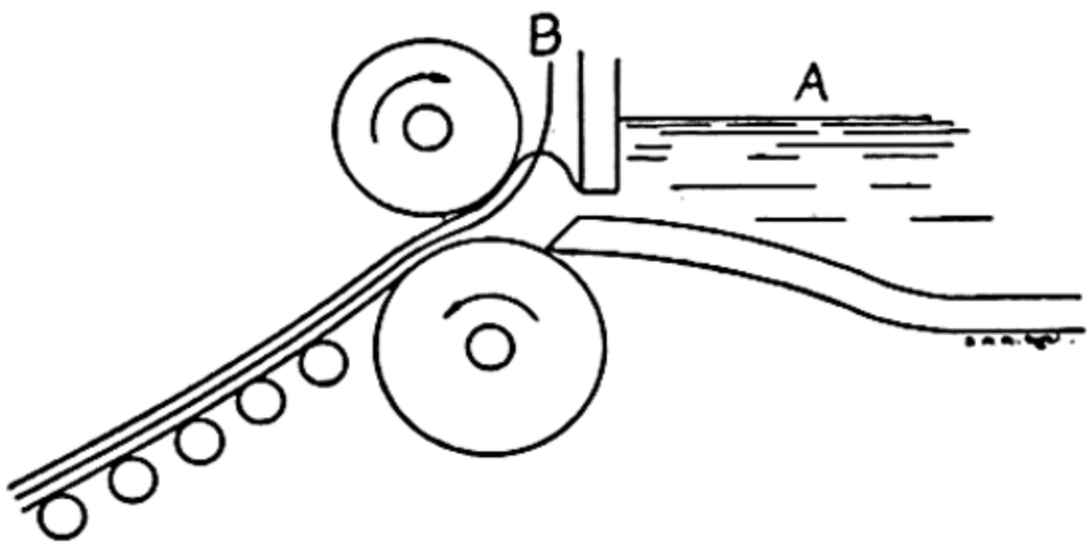


FIGURE 81.—Apparatus for the continuous drawing of wire glass. *A*, the glass furnace, working end; *B*, sheet of iron wire.

cooling in the lehr, the inner cell is under reduced pressure. Walls and windows made of glass blocks cause no condensation on the inner side of the wall in cold weather; in the hot season, they reduce the glare of the sun without the help of curtains or shades. The blocks are laid with a portland cement mixture, and the courses stiffened by means of two iron rods laid in the cement. Large wall sections such as 20 feet wide by 14 feet high are built rigid at the base, on a sill of concrete, and "float" on the other three sides. Glass blocks have a high insulating value against both heat and cold, and readily permit air-conditioning of factories and homes in hot climates.

Optical Plate Glass. Plate glass of good optical quality is made by melting a glass batch in clay pots and stirring the glass to form a homogeneous melt. The glass is then poured on a table and rolled flat. The plate is cut into smaller sizes and may be remelted in a small clay mold. The older method of making optical glass is the cooling-pot method, in which the clay pot filled with the melted glass is transferred into cabinets which are cooled gradually and at a slow rate. The cooled pot and its contents are broken into fragments, from which fragments without defects are selected by hand, and melted over in small molds. About 75 per cent of the glass is rejected. The optical plate method avoids the destruction of the pot, and only 20 per cent of its product is rejected, but its use is limited to certain purposes such as spectacles.

A still different method of avoiding pot destruction is the continuous tank furnace lined with platinum, and heated by graphite electrodes dipping into the melt. The glass is extruded in the form of bars which are later remelted. Platinum pots have come into use for melting the optical glass batch (except heavy flints).

[15] The wedding present sent Princess Elizabeth by President Truman was Steuben ware.

(3) Container Manufacture. Containers were formerly made by hand: a worker could produce 500 to 800 bottles a working day, for example. The method consisted of gathering a gob of glass at the end of the punty from the glass melt in the pot, removing it from the furnace, revolving it rapidly, rolling it against a flat slab, at the same time blowing gently, to work the glass into a hollow pear-shaped form. The partly shaped form was quickly

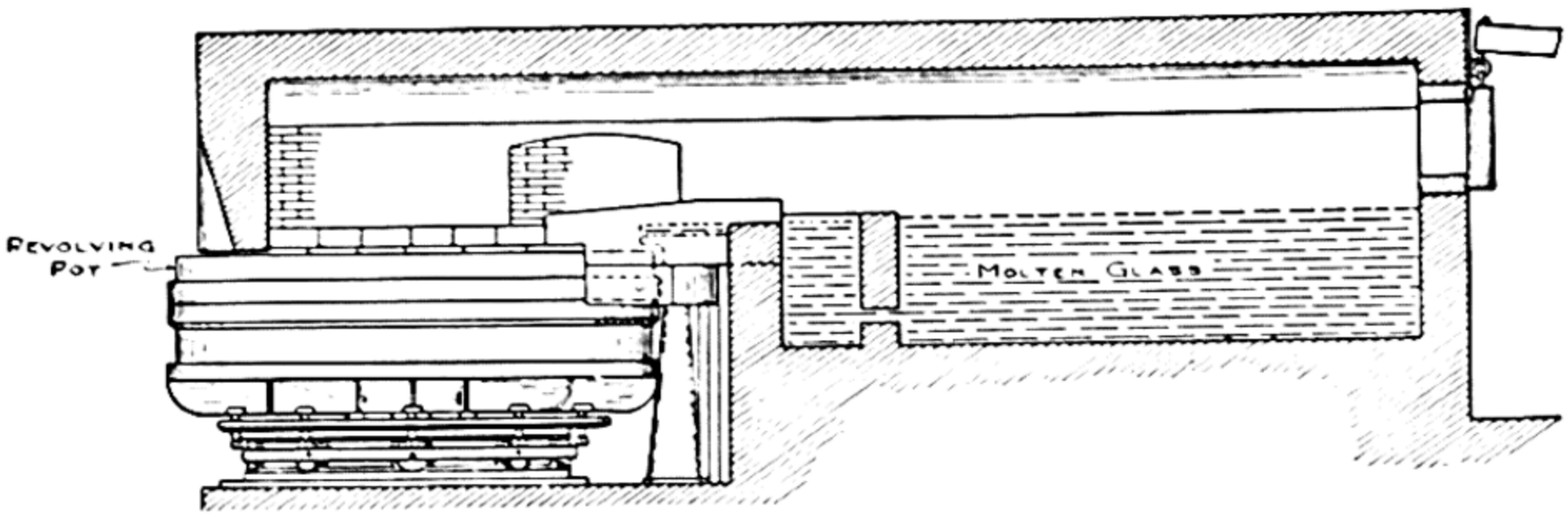


FIGURE 82.—The revolving pot for feeding the Owens bottle blowing machine.

placed in a hinged iron mold for the final blow. The mold was opened and the bottle placed in the lehr. Today, bottles are blown in automatic bottle-blowing machines at the rate of 6000 bottles per eight hours per machine, and less glass is required in the process.

Several automatic bottle-blowing machines have been developed. In the *Owens machine*, iron molds mounted on arms radiating from a central pillar revolve discontinuously, periods at rest alternating with motion. The mold passes over a revolving pot (9 feet or more in diameter) containing the

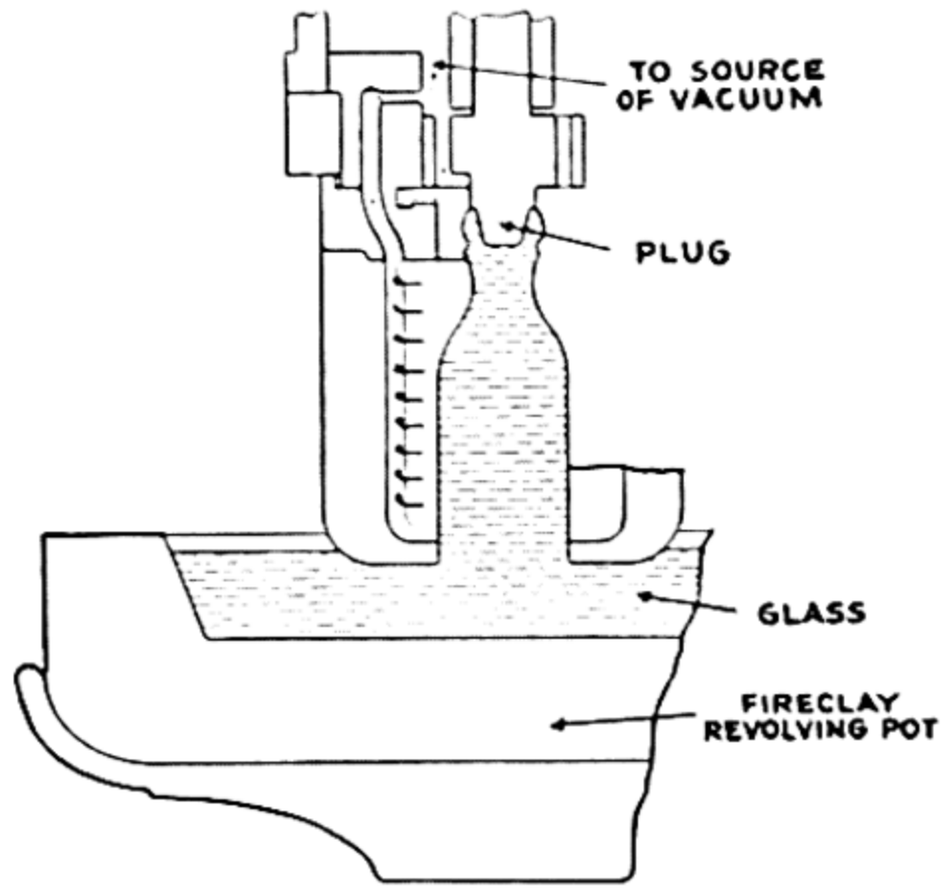


FIGURE 83.—Action of Owens machine in filling the mold by suction from the revolving pot.

glass melt and fed from a tank furnace; the arm lowers the mold, which sucks up a charge of glass and rises. A knife then cuts off the glass and closes the mold. The charge of glass has been forced against a plug which forms the opening which later becomes the neck of the bottle. After a blow of air, the "parison" mold opens and withdraws, and is replaced by a finishing mold, in which, after several other operations, the soft glass is

blown into its finished shape. The arm of the machine lifts the bottle and deposits it on a conveyor which enters the lehr.

A second type of automatic glass-blowing machine is the *Two Table Machine*, in which the parison and finishing molds are mounted on separate revolving systems (Lynch, O'Neill). The glass may be fed in the form of

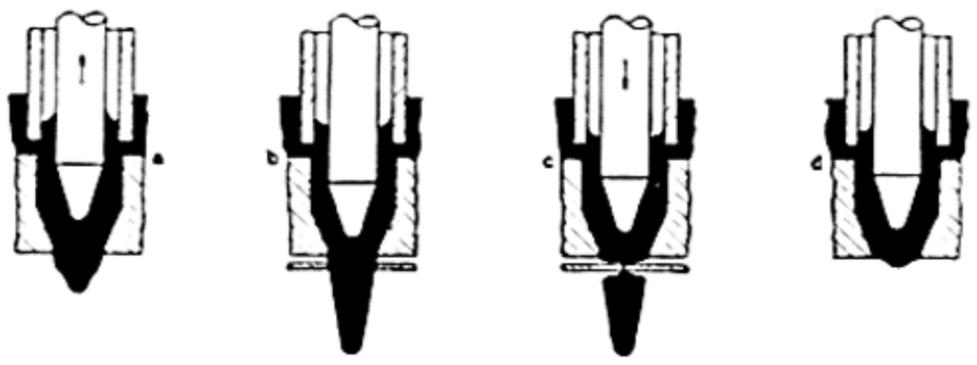


FIGURE 84.—Diagram of operation of the Hartford Single Feeder, which forms and delivers gobs of glass from the tank to the molds of the forming machine. At c, the gob is about to drop off; at d, the plunger has risen.

gobs which drop down into the first parison mold. In the Hartford feeder, a gob is formed each time the reciprocating plunger pushes glass out through an orifice in the floor of the forehearth; suspended mechanical shears cut off the gob at the right moment. A blow forces the glass against a plug,

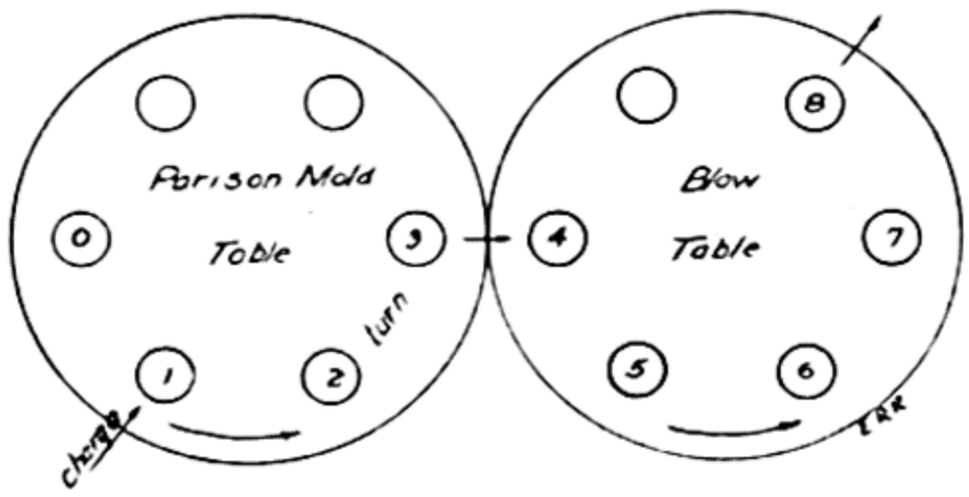


FIGURE 85.—Automatic glass bottle-making machine: the two revolving tables.

forming the depression which a step further, by a blow of air from below, forms the cavity. The parison so formed is turned bottom side up, and transferred, without its mold, to the second table. Here a blow mold closes around it, and after a period for reheating, a further blow shapes the bottle.

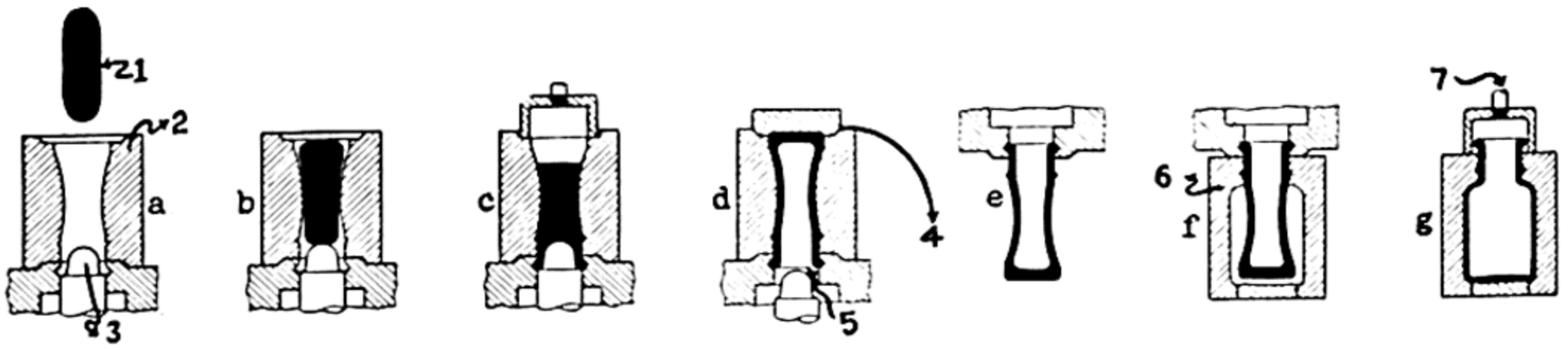


FIGURE 86.—The blow and blow process of forming a bottle, with gob feed. The gob, at 1, drops into 2, the parison mold. At c, there is an air blow from above; at d, from below, the compressed air entering at 5. The parison mold turns at 4 to position e. Finishing mold is shown at f and g; compressed air enters at 7 for the final blow.

The adjoined figures will make the operation clearer. A bottle-blowing machine is complicated, and precise timing of the blowing operations is essential.

An example of a furnace which supplies glass for a Two Table Machine is as follows: The plant manufactures a blue bottle for a popular pharma-

ceutical product and requires 27 tons of glass a day. The charge consists of 1000 lbs. of sand, 380 lbs. of soda ash, 100 lbs. of feldspar, 140 lbs. of lime (CaO), and 800 lbs. of cullet; for these 2420 lbs., 1 lb. of cobalt oxide (CoO) furnishes the attractive blue shade. The furnace is fired by oil (72 gallons of oil per ton of glass). A major improvement in construction is the triangular doghouse which, with especially designed measuring feeders, permits the automatic distribution of islands of batch into the furnace according to a predetermined pattern, resulting in better quality of product and greater yield per furnace.[16] From the melting end, the glass passes to the refining end, with 6 forehearths, in each of which a gob-feeder moves up and down, discharging a gob of glass which is cut off by mechanical shears. The gob drops into a funnel which guides it to the parison mold marked "a"

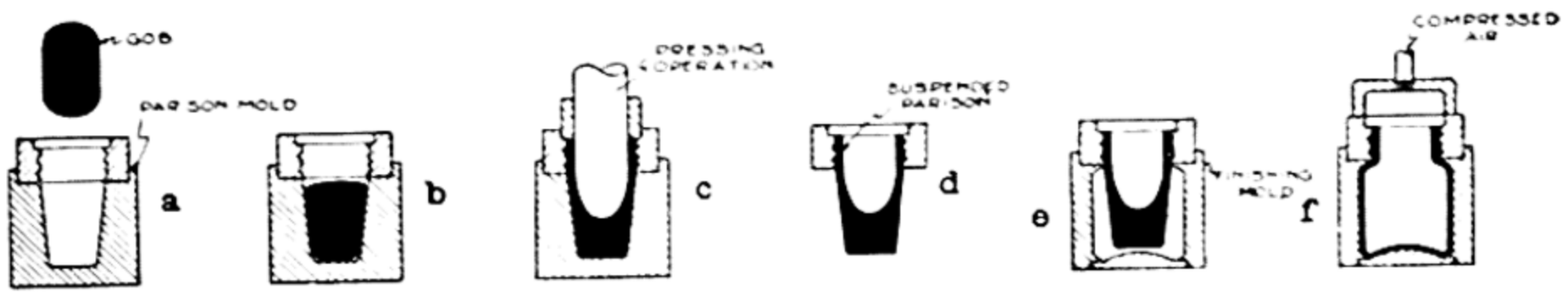


FIGURE 87.—The press and blow process of forming a bottle, with gob feed. The pressing operation is shown at c; until the parison is suspended in the finishing mold at e, it has received no air blow. Air is applied at f.

in Figure 84. The charging of the furnace is continuous, so that the level of the glass melt is strictly stationary, insuring regularity of feed to the blowing machines.[17]

The discharge from the second table is onto a conveyor, from which a mechanical arm picks up the bottles one by one and places them, spaced irregularly, onto a moving platform which travels through the lehr for the annealing period. The rate of production is 1 bottle in 4 seconds, or 900 an hour, for each machine.

An ordinary bottle may show a thick zone about two-thirds of the way down, marking where the parison ended. A line just under the neck marks the mold for the "finish." Two vertical lines may be seen on each side, the first and very faint line marking the halves of the parison mold, the other the halves of the blow mold. A line near the bottom indicates the blow piece at step 4.

In the *Press and Blow Process*, a container is partly shaped, first by pressing, then by blowing. An example is shown in Figure 87.

Pressed glass is shaped without the aid of an air blow into plates, fruit dishes, candy dishes, and other table pieces. Pressed glass pieces with original designs, pressed by hand, most of them made many years ago, are highly prized. Today, the process is mechanized.

[16] "Hartford develops new system of glass melting," *Glass Industry* (February, 1941) with a chart showing typical settings of the timing dials.

[17] For a picture and further description of automatic bottle blowing machines, see "Textbook of glass technology," F. W. Hodkin and A. Cousen, London, Constable & Co., Ltd., 1925; New York, D. Van Nostrand Co.

(4) The Danner Process. In the Danner process for making glass tubing, glass from a tank furnace or from hooded melting pots is ladled into the Danner furnace pot, a covered pot set in a muffle furnace.[18] The design of the pot is complex: there is an internal wall, with an opening at the base, so that scum-free glass from the pot overflows into a rectangular trough which ends in a flow lip. A level indicator helps to make an accurate adjustment of the glass level in the trough. A glass stream of constant and selected temperature is delivered at the lip to an inclined, revolving

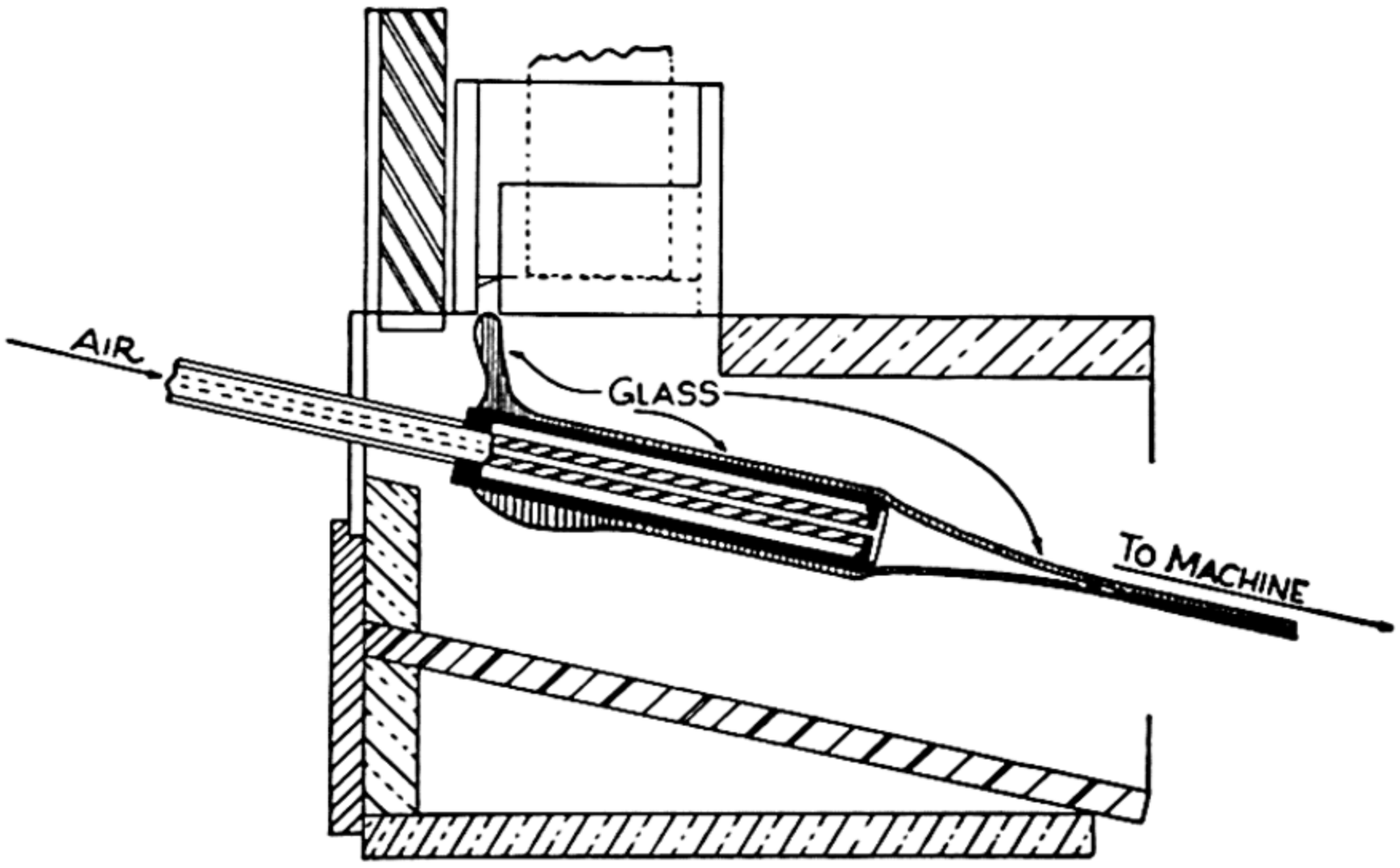


FIGURE 88.—In drawing tubing, glass flows from the tank onto the rotating cylinder, thence to be drawn by the Danner machine. (Courtesy Kimble Glass Co., Toledo, O.)

blow pipe, in such a way that the ribbon wrapped around the blow pipe slowly slides down it and finally flows off the head. The air under pressure fed to the blow pipe prevents the tube from collapsing until it is rigid. The tubing travels horizontally on the runway (150 ft long), over asbestos-covered aluminum pulleys, pulled by a drawing machine whose two asbestos-covered caterpillar chains touch the tubing for a distance of 3 feet. Part of the runway is shielded and acts as a lehr. At the end of the runway, the tubing is cut into lengths of 5, 6 or 10 feet by a revolving cutter block. The larger sizes are end-glazed. The linear rate of draw varies from 16 to 900 feet a minute, the higher speeds for the smaller diameters. The inside diameter and the wall thickness are regulated by the adjustment of a number of variables. Among these are the viscosity of the glass, which is itself regulated by the temperature for a given melt; the angle of inclination and the rate of rotation of the blowpipe; the pressure on the air; the amount of glass fed to the pipe, and the rate of draw. Both soda-lime glass and lead glass are made into tubing; among the several varieties of the former are a mercury-resistant glass, and a yellow opalescent tubing.

[18] "The automatic production of glass tubing and rod on the Danner machine," V. E. Sibilia, *J. Soc. Glass Tech.*, 23, 292 (1939).

The thick-walled, capillary tubing for thermometers is drawn on a vertical draw-up machine.

(5) The Corning Bulb Machine. In the Corning 399 electric bulb machine, a stream of soda-lime glass from the forehearth of a tank furnace drops between two cylindrical rolls.[19] One roll is smooth, but the other has numerous regularly spaced pockets on its surface. As the rolls rotate toward each other, there are formed small masses of glass, each sufficient to form one bulb, united by a thin, continuous sheet of glass. The plastic ribbon drops onto a series of orifice plates on an endless chain, moving horizontally; each small mass fits exactly into an orifice. A nozzle is dropped from above on each orifice, and an air blow elongates the mass into a sack. Next, the two halves of a mold meet and close about the sack; the mold is revolved at a rapid rate; two short blows then expand the glass to fill the mold. The nozzle lifts, the mold opens, its two halves traveling separately to a cooling-water spray before returning. A mechanical hammer strikes each bulb lightly but sharply, knocking it into one of the many asbestos-lined pockets mounted on a rotating wheel (with horizontal axis). In the meantime, the still-soft ribbon, now with many holes, is lifted from the orifice plate, sprayed into frit, and after drying is returned to the furnace. The actual blowing takes only a few seconds. The rotating wheel discharges its bulbs into a lehr, at the end of which they are examined.

For each size and style of bulb there is an assembly of orifice plates, molds, and nozzles. The machines produce 500,000 bulbs in 24 hours.

Light passing through *frosted glass* is pleasantly diffused; this matt finish is produced by immersion in a bath containing hydrofluoric acid, and saturated with ammonium bifluoride, NH_4HF_2. Etching of a design may be done in the same way, except that the parts which are not to be etched are covered with paraffin. Electric light bulbs are etched on the inner side, while set on racks, 100 at a time, by squirting the solution from below into the bulb.

Glass-making Refractories

Supplementing the information given in this chapter on refractory bricks and shapes, a reference [20] is listed below which gives a detailed description of refractories for bottle-glass furnaces, and for flat-glass furnaces, with a classification for each. The reference contains numerous sketches of furnace, forehearth, and revolving pot for the Owens machine.

Miscellaneous Recent Developments

"Fiberglas." "Fiberglas" is glass reduced by a mechanical process to a flexible thread or filament. By throwing a thread of glass, pulled from a heated glass rod, over a rapidly revolving drum, the glass is drawn into fibers resembling wool or silk; such threads are woven into cloth of various

[19] "Automatic glass blowing," D. H. Killeffer, *Ind. Eng. Chem.*, 28, 789 (1936).

[20] "Industrial survey of refractory service conditions in the glass industry. Part I, Continuous bottle glass furnaces. Part II, Continuous plate glass and window glass furnaces," p. 159-175, Manual of A.S.T.M. Standards on Refractory Materials. June 1943, A.S.T.M., Philadelphia, Pa.

kinds which serve useful purposes, comprising an inorganic textile industry. Besides the continuous filament "Fiberglas," a staple fiber is produced. One method is as follows: A stream of glass drawn from the forehearth of a melting furnace is allowed to cool and harden to a wax-like consistency, and is then directed while still hot into a metal layer machine, wherein it is fused by an oxy-acetylene flame and blown by compressed air into fibers gathered in a collecting room. Another method provides a gas blast within the furnace which syphons the molten glass upward to a glass terminus from which it is blown into a collecting chamber.[21] In still another process a stream of fluid glass is allowed to flow downward through an electrically heated platinum nozzle upon a rapidly revolving refractory disk.[22] The resulting centrifugation produces threads that are long and short, twisted together, so that the product has been designated as "glass wadding."

For staple fiber in general, the length averages 10 to 12 inches, the diameter in the latest procedures being 0.007 millimeter (0.00028 inch). The continuous fiber is made as thin as 0.005 millmeter (0.00022 inch). The most widely used method of making staple glass fiber consists in the use of multiple orifices of platinum through which molten glass is drawn by suction. The latter is induced by steam jets placed at the proper angle near the exits of the orifices. In the form of a felted mass, "Fiberglas" is an excellent thermal insulator, which has become almost standard in house and warship construction. Its thermal coefficient is only 0.266 Btu. per square foot area per inch thickness per hour per °F.

"Fiberglas" draperies in colors are invading the decorative textile field; their popularity will not suffer because they are fireproof. Fabrics composed of 60 per cent glass fibers and 40 per cent cotton are available. "Fiberglas" yarns coated with a thin gelatin film may be dyed with ordinary dyes. Vinyl-coated "Fiberglas" fabrics are recommended for outdoor furniture.[23]

"Fiberglas" as a distilling column packing is giving good results.

Photosensitive Glass. There has been developed a photosensitive glass in which colored pictures may be produced by exposure through an ordinary black and white negative, followed by development.[24] The exposure is to ultraviolet light (sunlight, mercury arc, mercury lamp), and development is by heating in an oven to an elevated temperature, such as 1000° F. (538° C.). The glass is a high alumina soda-lime silicate glass, prepared according to any one of several batch formulas. All the formulas contain at least 0.05 per cent of Cu_2O and a reducing agent, but differ in the nature of the latter which may be sodium cyanide, abietic acid, or both. Another addition is stannic oxide. The positives produced in the photosensitive glass give a three-dimensional effect; they are durable, possess fine detail, and have a variety of color, which depends upon the glass composition. Glass made with sodium cyanide as reducing agent and without tin oxide

[21] U. S. Pat. 2,175,225 (oxy-acetylene flame); U. S. Pat. 2,156,316 (platinum nozzle).

[22] "The manufacture, processing, and use of glass fibers," by G. V. Pazsiczky, translated from Glastech. Ber., June, 1936, by Dr. Samuel R. Scholes, The Glass Industry, 18, 17 (1937) [11 W. 42, New York].

[23] *American Glass Review*, 66, No. 41, 28 (July 5, 1947).

[24] U. S. Pat. 2,326,012, Glass article, and 2,422,472, both to Robert H. Dalton, and assigned to the Corning Glass Works, Corning, N. Y.

permits the production of blue; inclusion of tin oxide with abietic acid as the reducing agent, or the cyanide, gives a glass which produces images in red; other modifications permit the production of pictures in yellow and brown. The negative employed must itself transmit the active radiation; or, alternatively, a sheet of the photosensitive glass may be coated with a special photographic emulsion, the negative image developed in the usual way, and the glass then irradiated with ultraviolet light, followed by development in the oven, producing the positive, permanent image in the glass, in the color corresponding to the type of glass selected.

Other Glasses. Cellular glass is made by mixing finely powdered glass with carbon. When the mixture is heated above the softening temperature of the glass, a reaction between the carbon and sulfate in the glass produces myriads of minute bubbles in the mass. The resulting foam is allowed to cool. It is black and has a sponge-like appearance, and weighs only 10.5 lbs. per cubic foot. It is a heat and sound insulator.

Silica aerogel has been in use as an insulator for some time.[25]

Some of the recent developments have been given in the preceding pages. Constant trials, study, research and invention increase the usefulness of glass, the number of its applications, and lower the price.

In the optical field, lenses have been coated with magnesium fluoride in order to diminish reflection, and hence increase transmission. On the other hand, the reflection can be increased by special coatings, thus forming "one-way vision" glass.

Production. The extent of the glass industry is indicated by the volume of shipments, as shown in Table 38a.

TABLE 38a.—*Quantity and value of shipments, glass industry.**

	1947		1939
	Quantity	Value	Value
Sheet glass, boxes of 50 sq. ft.	18,900,000	$ 72,500,000	
Obscured glass in sq. ft.	64,200,000	9,700,000	
Wire glass, sq. ft.	30,400,000	5,600,000	
Plate glass, laminated, structural opaqued glass, multiple-glazed sealed insulating units, others		155,000,000	
Glass containers, gross pieces	111,200,000	415,700,000	151,000,000
Pressed and blown glassware, other than containers, other products		6,900,000	6,700,000

* Bureau of the Census, Industry Division, Minerals Section.

OTHER PATENTS

U. S. Patent 1,880,540, electric furnace for melting glass and new type of electrodes for such a furnace; 1,920,366, drawing thermometer tubing; 1,838,162, apparatus for producing glass tubing; 2,064,361, spectacle glass composition to give a faint pink shade; 2,056,627, ultraviolet transmitting glass; 1,852,218, apparatus for feeding molten glass; 2,005,494, feeding glass by alternate application of pressure and vacuum; 1,999,562, continuous production of "plate" glass with one rough and one fire-polished surface; 2,012,583, method of manufacturing bottles; 2,030,810, glass forming and gathering machine; 2,045,716, apparatus for casting large telescope disks; 2,053,902, furnace for melting glass; 1,981,636, making lamp bulbs from tubing; 2,034,925, hollow glass building blocks; 1,788,312 and 2,069,130, on glass blowing machines; 1,970,354, on means

[25] "Manufacture of silica aerogel," John H. White, *Trans. Am. Inst. Chem. Eng.*, 38, 435 (1942).

for feeding glass to the blowing machine; 2,176,654, improved type of glass wall construction; 2,176,012, a vacuum bottle; 2,091,691, on glass compositions. U. S. Patent 2,244,113,—2; 2,268,609; 2,284,832; 2,335,128; 2,151,983; 2,133,783,—4; Re 19,074, on lehrs; 2,072,826; 1,905,476, on stackers; 2,139,911; 2,139,770; 2,073,572,—3, on feeders; Re 19,439, original 1,896,870.

Problems

1. Compute the total number of square feet of floor area in the tank furnace described in the text, with the melting end 52 feet by 26 feet included. Where dimensions are missing, scale the drawing, for it is made to scale. Each one inch of height of glass is equivalent to 21.5 tons of glass. What is the apparent specific gravity of the glass melt from this relation? What is the total capacity of the furnace, to a height of 60 inches?

2. If 60 tons of glass per 24 hours are drawn from the furnace described in Problem 1, how long does any one pound of glass spend in the furnace?

Note: This estimate should be made first on the basis of the calculated capacity, in order to indicate the magnitude of the movement. In reality, only the upper 10 to 16 inches of the melt moves and it is this layer which furnishes glass for the daily withdrawal, so that the rate of movement is faster than first computed. Base other estimates on movement of 10-inch layer, then 16-inch. The higher the temperature, the deeper the layer which moves. The lower immovable portion is colder and hence more viscous.

3. The materials charged into the furnace every 20 minutes are given in the text. The shrinkage due to loss of CO_2 and SO_3, calculated on the basis of pure materials, would be how much? Express in terms of percentage of the total charge. Compare with the figures given in the text.

4. What will be the molecular formula of the glass? (Divide parts by weight by the molecular weight of the oxide, tabulate quotients, and divide by the smallest.)

5. Examine a number of bottles for the telltale lines indicating the steps in the automatic blowing operation as described in the text.

Reading References

"Properties of Glass," G. W. Morey, New York, Reinhold Publishing Corp., 1938.

"A textbook of glass technology," F. W. Hodkin and A. Cousen, London, Constable & Co., Ltd., 1925, New York, D. Van Nostrand Co.

"Continuous process for plate at Ford River Rouge plant," E. P. Partridge, *Ind. Eng. Chem.*, 21, 1168 (1929).

"Manufacture and characteristics of laminated glass," Willard L. Morgan, *Ind. Eng. Chem.*, 23, 505 (1931).

"The manufacture of optical glass and of optical systems," Lieut-Col. F. E. Wright, *Ordnance Dept. Document*, 2037, 1921.

"Jena glass and its scientific and industrial application," Hovestadt, translated by Everett, New York, Macmillan Co., 1902.

"An investigation of selenium decolorising," E. J. Gooding and J. B. Murgatroyd, *J. Soc. Glass Techn. (British)*, 19, 42-103 (1935).

"The 200-inch telescope disc," George V. McCauley, *J. Soc. Glass Technology (British)*, 19, 156-166 (1935), with numerous illustrations; also published in *Bull. Am. Ceramic Soc.*, 14, 300-322 (1935).

"Defects in glass," C. J. Peddle, London, *Glass Publications, Ltd.*, 1927.

"Modern glass practice," Samuel R. Scholes, Chicago, Industrial Publications, Inc., second edition, 1940.

"Feldspar as a constituent of glass," edited by Donald E. Sharp, New York, National Feldspar Association, 1937.

"The behavior and misbehavior of glass in tanks," F. W. Preston, *Bull. Am. Ceram. Soc.*, 15, 409 (1936).

"The manufacture of rolled plate," Ernst Lutz, translated from the German, *Glass Industry*, 11, 227, 255, 277 (1930), and continued through 1931 to 1932, in installments, a comprehensive treatment.

"Chromium plating glass molds," D. McGregor, *Am. Machinist*, 85, 854 (1941).

"Recent trends in glass composition," Donald E. Sharp, *Glass Industry*, 21, 158 (1940), with a bibliography.

"Chemistry and vitreous enamels," Emerson P. Poste, *Ind. Eng. Chem.*, 32, 9 (1940).

"Nepheline-Syenite, a new mineral which is competing with feldspar," *Pit and Quarry*, p. 70, January, 1940.

"Modern processing of feldspar," J. H. Weiss, *Ind. Eng. Chem.*, 26, 915 (1934).

"Fiberglas, a new basic raw material," Games Slayter, *Ind. Eng. Chem.*, 32, 1568 (1940).

"Glass, the miracle maker," C. J. Phillips, New York, Pitman Publishing Corporation, 1941.

"Fiber Glass, mechanical development," J. H. Plummer, *Ind. Eng. Chem.*, 30, 726 (1938).

"Low-pressure laminating of plastics," by J. S. Hicks; New York, Reinhold Publishing Corp., 1947. (Chapter 4, on glass reinforcements).

"Flat glass and related glass products," Second Series Report No. 123, United States Tariff Commission.

The industrialist deals not only with raw materials and products of reactions, but also with fuels, steam, and electrical power; frequently it is the cost of these rather than of raw materials or investment in physical plant which determines whether a certain enterprise shall be continued or given up. Hydroelectric power and steam-generated power supplement each other. Unlike steam power, hydroelectric power does not reduce our finite store of coal, in which respect it has an advantage; on the other hand, if the hydro plant is at some distance from the center of consumption, its performance suffers through the loss in transportation of even high-tension current over distances of no more than 100 or 200 miles, so that in this way, the locally erected steam power plant has an advantage.

Chapter 12

Fuels, Steam Boilers, Hydroelectric Power, Steam Power, and Production of Cold

There are only a few industrial chemical processes—sulfuric acid manufacture, for example—in which fuel is unnecessary. By far the greater number of processes require fuel, or heat produced by resistance to an electric current. High temperatures, in the neighborhood of 1000° C., are reached by the direct application of fuel, as in the reverberatory furnace.[1] More moderate temperatures, about 100° C., are conveniently reached and maintained by means of steam in jackets, in coils, or led directly into the reacting mixture (wet steam). Soft coal is the important solid fuel at present; the term includes bituminous and semi-bituminous coal. Anthracite [2] has only slight importance for the chemical and allied industries; soft coal is more abundant,[3] cheaper, and in many cases is preferred because of its long flame. For the manufacture of coal gas, only bituminous or semi-bituminous coal is used; if the coal is of the coking variety, there is left in the retort another valuable semi-manufactured fuel, coke.[4] This is the most suitable fuel for iron blast furnaces and similar processes, for its hardness and strength enable it to carry great loads without being crushed. Pulverized soft coal burns like a gas. Liquid fuel is chiefly "fuel oil" [5]; it is burned under boilers, in furnaces of all kinds, and to a smaller extent in Diesel engines,[6] internally. Gasoline [5] is a specialized fuel, used for internal combustion motors. The gaseous fuels [7] besides coal gas are natural gas, water gas, butane, propane, and producer gas; for the production of the latter, lignite [8] may be substituted for the soft coal usually used.

[1] *Compare* introduction to Chapter 17.

[2] The one important anthracite area in the United States is northeastern Pennsylvania (Scranton, Wilkes-Barre, Mauch Chunk).

[3] There are about 400 anthracite and 9000 soft-coal mines in the United States.

[4] Chapter 14.

[5] Chapter 24.

[6] The Diesel engine has no spark plug; ignition temperature is reached by compression (500 pounds).

[7] Chapter 15.

[8] Lignite contains water; the extensive deposits in the West will probably not be worked intensively until coal is exhausted, except for local needs. North Dakota lignite is being mined now (1937) and utilized for making gas and briquet fuel.

A comparison of the heat value [9] of the several fuels is given in Table 38b.

TABLE 38b.—*Comparison of heat values of various fuels.*

Anthracite, fixed carbon about 87 per cent	per pound	13,500	B.t.u.
Bituminous coal, fixed carbon about 60 per cent	" "	14,400	"
Coke, fixed carbon about 92 per cent	" "	12,900	"
Wood, dried	" "	8,000	"
Charcoal	" "	12,800	"
Fuel oil	" "	18,500	"
Kerosene	" "	20,000	"
Natural gas	per cubic foot	1,100	"
Coal gas	" " "	600	"

It is evident from this table that bituminous coal is a high-grade fuel. It occurs in almost limitless quantities in the United States; a recent estimate is three and a half trillion tons, counting all types. The deposits in England [10] are next in importance; then come those in France, Russia, Germany, and Belgium. Within the United States, western Pennsylvania and West Virginia lead [11]; other eastern and southern states with important outputs are Virginia, Maryland, Tennessee, Alabama. In the middle west. Ohio, Illinois, Indiana, Iowa, Missouri, and North Dakota have important coal resources; farther west, Wyoming, Colorado, Utah, New Mexico, Oklahoma and Washington. Coal is generally agreed to be of vegetable origin.[12]

Production and prices were as follows:

	1947	1948 (prel.)
Production, bituminous coal and lignite	630,623,722	594,000,000 net tons
Cost of railroad fuel, f.o.b. mines	$3.64	$4.34
Cost of coking coal at merchant coke ovens	7.43	9.00
Average retail price	12.99	15.40
Average railroad freight charge per ton	2.49	2.71
Average value f.o.b. mines	4.16	4.95
Surface stripping production	139,395,011	138,000,000
Mechanically loaded underground	298,157,281	286,000,000
Mechanically cleaned	174,435,937	175,000,000
Pounds of coal/kilowatt hr. at electric power plants	1.31	1.30
Production of anthracite	57,190,000	57,052,000 net tons

(Bureau of Mines, Mineral Industries Survey.)

[9] British thermal unit, the heat required to raise 1 pound of water 1° F.; it takes 4 Btu. to equal 1 large Calorie, the heat required to raise one kilogram of water 1° C. (at 18° C.).

[10] The British coal fields are: *a*. The southern fields, including South Wales and Monmouth, partly under the sea; the coal is of all varieties, bituminous, anthracite, and intermediate; the seams are rarely over 3 feet in thickness, usually less. *b*. The central fields, North Wales, Yorkshire, Derbyshire, which yield coking bituminous. *c*. The northern fields, Scotland, Durham, which give good coking coal. The Ruhr district gives mainly coking bituminous. The basin in Northern France adjoins and in fact is part of the Belgian field; the coal is bituminous of all varieties. The Saar Valley coal is non-coking.

[11] Production in millions of tons in 1946 (Bureau of Mines, Mineral Market report No. 1558): W. Va., 144.0; Pa. (bit.) 125.5; Ky., 66.5; Ill., 63.5; O., 32.3; Ind., 21.7; Ala., 16.2; Va., 15.5; Wyoming, 7.6; U., 6.0; Col., 5.9; Ten., 5.16; total bituminous and lignite 533,922,000 net tons. Pennsylvania anthracite 60,507,000 net tons

[12] Vegetation, peat, lignite, soft coal and anthracite form a series of substances which

The chart (Figure 89) shows the ranks of coal, with composition, heat value, volatile matter, fixed carbon and moisture.

The methods of mining differ greatly. In the Pittsburgh district, there is a five-foot seam near the surface, so that no shaft is necessary, but merely

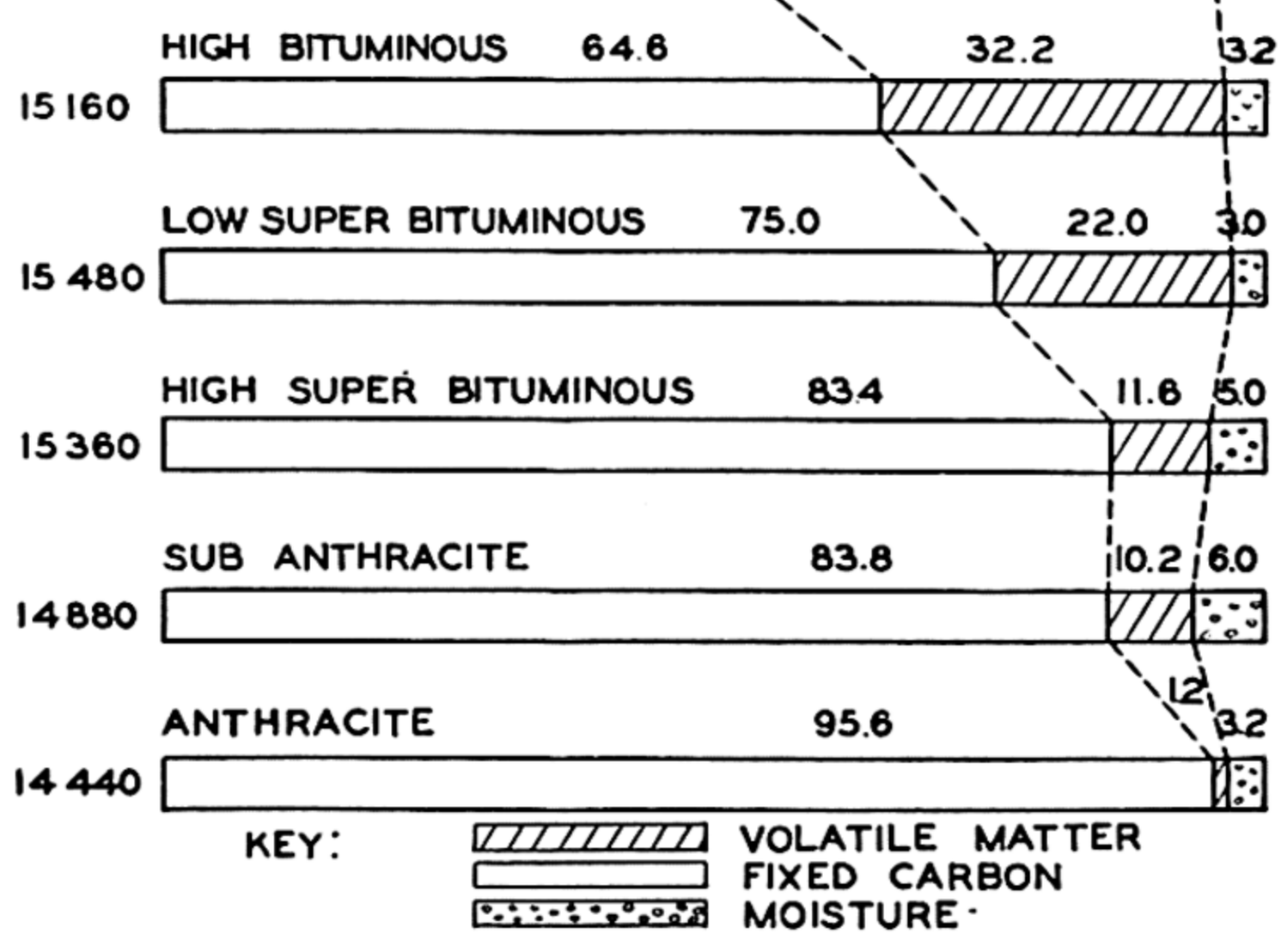


FIGURE 89.—A chart showing composition and heat value of the various kinds of coal.

inclined tunnels. This is mined in the following way: "Rooms," 250 feet deep and 20 feet wide, are marked out and the coal removed, leaving a wall between the chambers; a coal pillar must also be left around any oil-well

---

grade one into another in an unbroken line, reaching from complex organic, oxidized compounds at one end to nearly but not quite pure carbon at the other. Coal originated from vegetation which grew in swampy or marshy places. As the vegetation died it underwent a partial decay and was buried under successive layers, either of matter like itself or sediments like clay; it was subjected to a gradually increasing pressure while protected from atmospheric oxidation, and to some heat generated by the load and pressure. Coal is "chiefly composed of residues consisting of the most resistant components of plants such as resins, resin waxes and higher fats, or of derivatives of the compounds composing them."

casing reaching to the oil-bearing strata underneath. Within the "room" the cutting of the coal is done by electrical machinery and dynamite. The cutter, a low steel truck carrying two motors, travels on narrow-gauge tracks in the tunnels to the room ready for a cut; within the room, it is hauled on

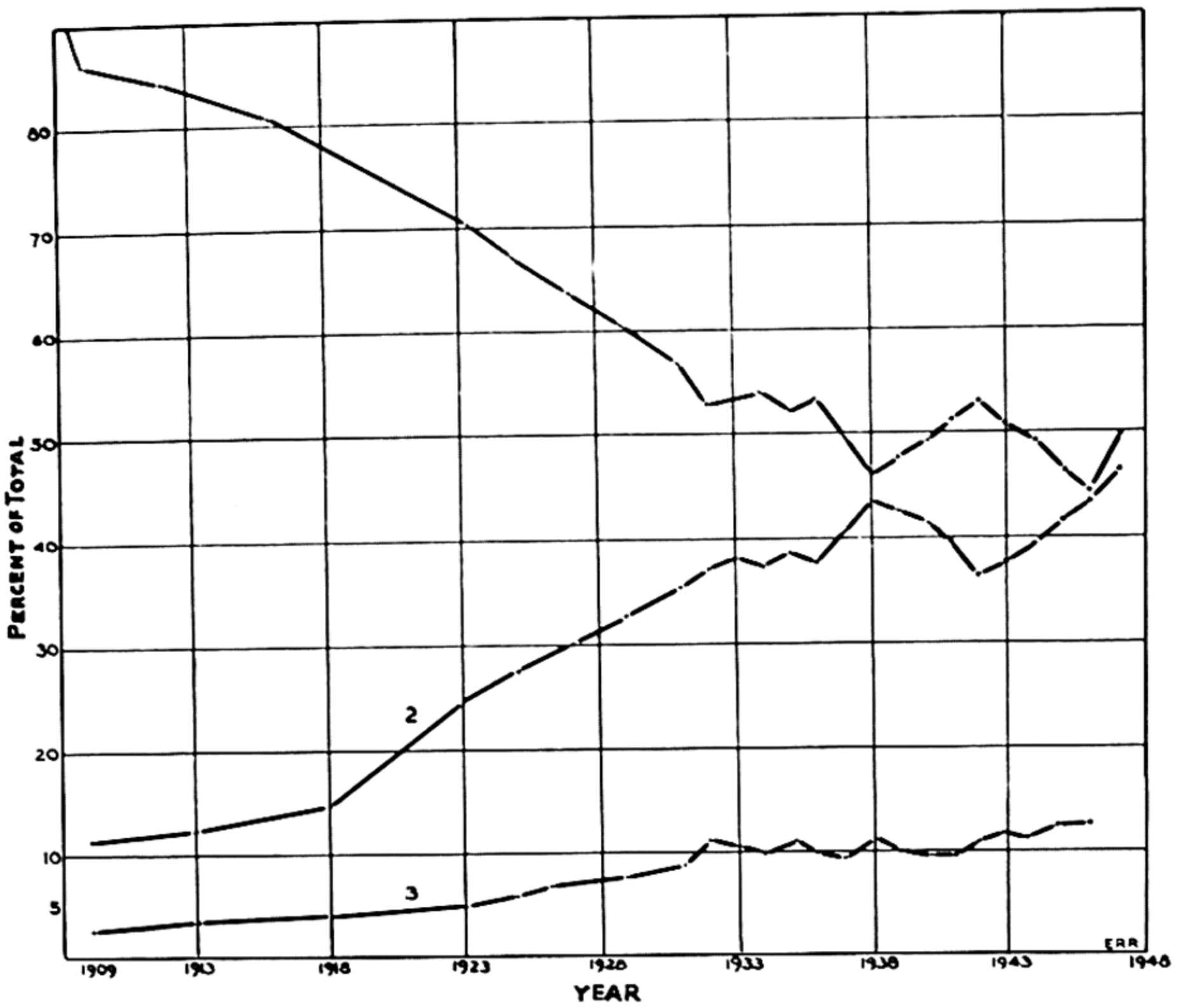


FIGURE 90.—Curves showing the relative importance of the several sources of energy over a period of years. Curve 1, coal; 2, petroleum oil and natural gas; water power. 3. The sharp drop in coal and equally sharp rise in oil and gas is well shown, to 1932; since then, the lines are roughly parallel. The water power is converted into its coal equivalent by accepting a unit consumption of 4 pounds of coal for each kilowatt hour. (Figures from Bureau of Mines, Coal Economics Division and Minerals Yearbook.)

timbers, pulling itself by means of a steel cable, drum-wound, looped around a temporary brace jammed between the ceiling (the height of the room is the height of the seam, 5 feet) and the floor. The cutter has a 9- or 10-foot tongue close to the floor; an endless chain carrying short, stout knives travels along its edges, actuated by a sprocket wheel driven by the motor. Power is taken by a flexible drum-wound cable from the copper lead in the tunnel. The tongue is allowed to penetrate into the wall close to the ground, cutting away the coal. The fine coal is swept out by the knives; during this operation, the cutter is hauled close to the wall by the cable, and this pressure forces the knived belt of the tongue inward. With the tongue all the way in, the belt continues running, and the cutter is slowly moved, again by its own cable, from one side of the room to the other, clearing a horizon-

tal space 6 inches high, 9 feet deep, and 20 feet wide. The cutter is now removed from the room by its two operators, and the miner takes charge; two or more holes are drilled into the coal, 5 feet deep, and set close to the ceiling; they are filled with dynamite and fired. In nearly every case the whole block, 5 feet by 6 feet by 25 feet, is tumbled down.[13] The miner with his helper loads the coal on the low mine cars and these are pulled out by an electric locomotive, at high speed, to the breaker house or tipple where the coal is crushed somewhat, freed from fines, and loaded by gravity (the breaker house is elevated) into railway cars.[14] The loading of the mine cars is increasingly mechanical by means of portable belt conveyors or a conveyor with reciprocating motion.

Other methods of mining coal are by deep-shaft operations, and by open pit exploitation, when the coal seam is not far from the surface (40 feet, for example). The latter method is called strip mining. Of the total bituminous coal and lignite [15] mined in the United States in 1946, 112,963,717 tons (21 per cent) were strip-mined.

TABLE 39.—Distribution of the bituminous coal and lignite consumed domestically, by consumer class, 1946.*

	tons
Fed to beehive coke ovens	7,167,000
Fed to by-product coke ovens	76,121,000
For the railroads, locomotives and shops	110,166,000
Used by electric power utilities	68,743,000
For steel and rolling mills	8,603,000
For cement mills	7,009,000
For coal gas retorts	1,500,000†
For general manufacturing	118,659,000
To retail dealers	100,586,000
Colliery fuel	1,951,000
Total for 1946	500,386,000

* Mineral Market Report 1558. The total for 1945 was 12 per cent higher.
† Estimated; included in general manufacturing.

For household use, anthracite is preferred to soft coal,[15] at least in the areas not too far from western Pennsylvania. Its use has been made more attractive by the application of a spray of calcium chloride solution, which prevents the formation of dust. In 1946, there were produced 60,506,873 net tons of Pennsylvania anthracite, of which 63 per cent was obtained from deep mines, 21 per cent from strip mines (the highest to date), 14 per cent from culm bank. The average value at the mine was $6.85 a ton; egg, stove and chestnut were $9.38 to $9.42; buckwheat No. 4 size was $2.09.

[13] The lay-out of the room is so planned with reference to the structure of the coal that the blast finds the lines of weakness, and as a result the coal falls forward with minimum blasting.

[14] The Primrose Mine, Carnegie Coal Company, Pittsburgh, Pa.

[15] In North Dakota, which possesses no other fuel than lignite, this low-grade material is being mined, distilled in special patented retorts, furnishing gas to municipalities, and briquet fuel to the state and to neighboring states. The development of by-products is under intensive study. There were produced in the United States (1946) 2,667,619 tons of lignite, of which 96 per cent were mined in North Dakota, and 4 per cent in Texas, Montana and South Dakota; the average value was $1.68 (Minerals Yearbook).

"Blue coal" is anthracite sprayed with a suspension of finely divided ultramarine or "Celestial Blue" in water, followed by partial or complete drying.[16]

The average value of bituminous coal per ton, f.o.b. mines, in 1946, was $3.44. The value at the strip mines was $2.87, at underground mines, $3.59. In 1945, the average value for all bituminous coal was $3.06 per ton; in 1947, $4.16; in 1948, $4.95.

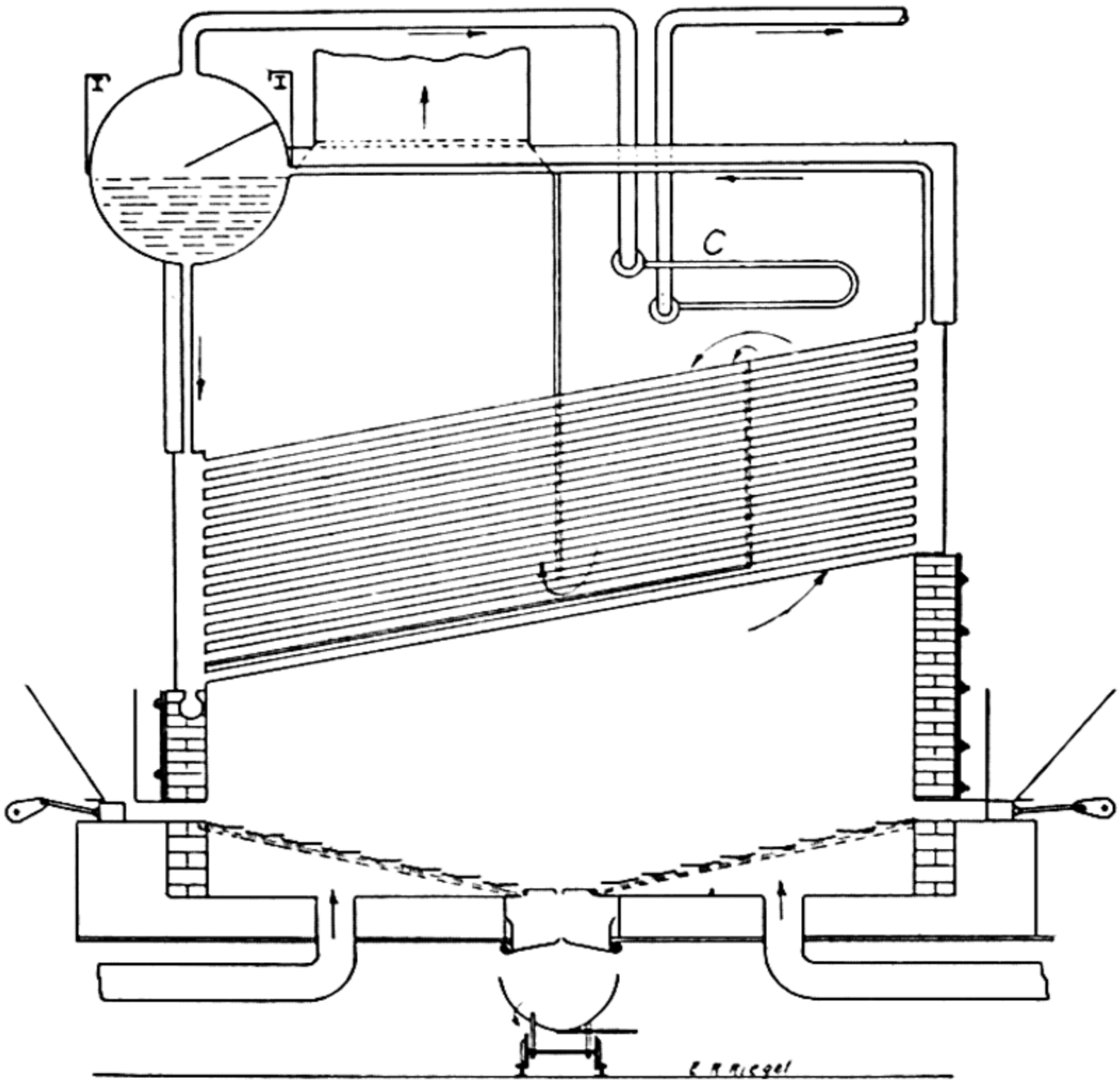


FIGURE 90a.—A water-tube boiler, with superheater at *C*. The circulation of the water and steam is shown, also the entry for the forced draft under the grate, the method of removing ashes, and the travel of the fire gases.

STEAM BOILERS

Stationary boilers fall into two classes: water-tube boilers, in which the water is inside the tubes, the fire gases on the outside; and fire-tube boilers, in which the fire gases pass inside the tubes, while the water is on the outside. Both types have one main drum or several drums which carry the greater part of the water. Locomotive boilers are fire-tube boilers; marine boilers of the older types are fire-tube boilers also, but most of the newer marine boilers are water-tube.[17]

Water-tube boilers are more efficient and safer; they are used for medium pressures, such as 200 and 275 lbs. steam pressure per square inch, as well

[16] U. S. Patent 1,688,695, to Dr. Gustavus J. Esselen; no adhesive is required.

[17] Compare *Marine Age* for December 1941, "A 1200-pound reheat marine installation," by Benjamin Fox and Richard H. Tingey, with discussion by W. W. Smith.

as for higher pressures, up to and even over 1,800 lbs. per square inch, as will be discussed more fully later. Their development is more recent than that of the fire-tube boilers. The Babcock and Wilcox, the Stirling, and the Heine boilers are water-tube. In Figure 90a, it may be observed that the fire gases strike the tubes at right angles; while in fire-tube boilers, the path of the fire gases is parallel to the tubes. The exchange of heat is more rapid with the former construction. An illustration of the fire-tube boiler is also given (Figure 91); it is cheaper in first cost, well suited to smaller plants, particularly for pressures of the order of 60 lbs. per square inch.[18] Both illustrations furnish a number of details. Vertical tube boilers, which may be of the transportable type, have fire tubes.

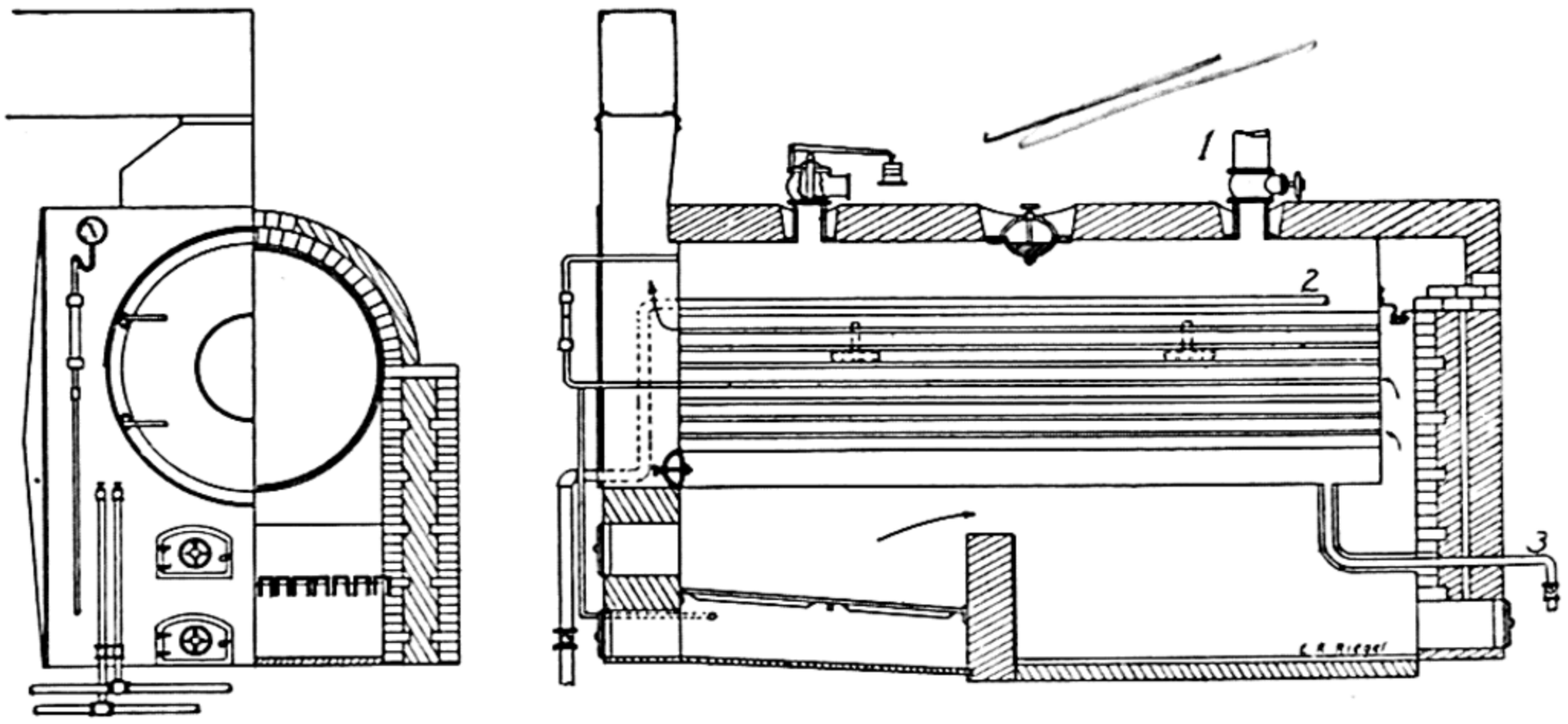


FIGURE 91.—A fire-tube boiler, with hand-fired grate. and natural draft; the steam leaves at 1; the feed water is delivered at 2; the blow-off cock is 3.

The material for the drums is mild steel, usually one-half inch in thickness, riveted; the tubes are rolled or spread to fit. In the superheater, shown in Figure 90a, the steam, after it has left the boiler system proper, is passed through a nest of pipes placed in the flue gases, where its temperature is raised 100 or more degrees above the boiler steam temperature. This treatment raises the work value of the steam, and is important for steam used in engines and turbines; for steam used for heating coils and jackets, such as the chemical engineer requires, it is less important, for it does not raise the heat value of the steam by very much.[19] For this reason it is common practice, in chemical plants having medium-pressure steam, to use superheated steam in a single-stage engine working for example between 275 and 40 lbs., and to use the exhaust steam for heating. In general, exhaust steam from pumps, engines, and compressors is collected

[18] If the steam must travel a long distance (2000 feet for instance), high-pressure steam is preferred, for smaller pipes will transport the same amount as larger pipes carrying low-pressure steam.

[19] Sixty-pound saturated steam has a heat content of 1177 Btu. per pound of steam; 60-lb. steam with 100° F. superheat has a heat content of 1227 Btu. The temperature of steam rises with rise in pressure; 60-lb. steam is 293° F.; 100-lb. steam 328° F.; 200-lb. steam 382° F.; the pressures are absolute. Marks, "Mechanical Engineers' Handbook," New York, McGraw-Hill Book Co.

in steam drums and fed from there to heating coils, sending fresh steam from the boiler into the drum only when the supply of exhaust steam is insufficient.[20]

Two steam boiler installations for chemical plants, both possessing a high degree of economy of operation and reliability for continuity, have been described in the literature, with illustrations.[21] In one plant, it had been found that autoclaves could use profitably steam at 250 lbs., while other processes needed steam at 125 lbs., and still others steam at 40 lbs.; the plant was to generate its own electric power. There were installed three boilers generating 260,000 lbs. of steam per hour, at 250 lbs. pressure, 406° F. (208° C.) for the saturated steam, provided with oil or pulverized coal firing interchangeably. Two 3500-kilowatt turbine generators were installed, and 40- and 125-lb. steam drawn off from their casings. In the other installations, a boiler generating 488-lb. steam was installed and run to give 400-lb. steam, whose temperature was raised to the required 725° F. (385° C.) by means of superheaters. The steam was applied to a turbine for power generation; the turbine delivered on its low-pressure side the 125-lb. steam which was required for the processes.[22]

For the development of high temperatures, diphenyl boilers, or diphenyl oxide boilers are in use. With a pressure of 144 lbs. per square inch (gauge pressure), a temperature of 750° F. (399° C.) is attained. The pressure is moderate, and the temperature may be maintained constant without any difficulty.

High-pressure steam boilers with high-temperature steam are discussed later in this chapter.

All steam boilers are now rated in terms of the pounds of steam generated per hour.

Water Softening. To prevent or at least minimize scale formation, the water fed to the boiler must be freed from dissolved calcium and magnesium salts. For water with carbonate hardness, containing calcium carbonate held in solution by carbon dioxide, milk of lime may be added, which will cause the calcium carbonate to precipitate. For water with non-carbonate hardness, containing calcium sulfate, soda ash is used. The treatment is best performed in separate vessels, and the water filtered by percolation through sand; or the softening chemical is sent directly into the boilers. In either case, the boiler must be blown once or twice a day, for the soluble

[20] The regulation is by means of a Locke damper or other regulator.

[21] "Cheaper power for the chemical industry," W. S. Johnson, *Ind. Eng. Chem.*, 23, 476 (1931).

[22] A variety of boilers is available, for example: A controlled radiant steam boiler with pulverized coal system, 1,000,000 lbs. of steam per hour capacity, at a pressure of 1,800 lbs., with steam temperature 955° F.; a type VM boiler with coal stoker, capacity 23,000 lbs. per hour, steam pressure 275 lbs.; type VA boiler, with multiple retort stoker, capacity 90,000 lbs. per hour, pressure 200 lbs., steam temperature 371° F.; type VU-Z boiler, with spreader stoker, capacity 38,800 lbs. per hour, pressure 275 lbs., steam temperature 505° F.; type VE boiler, traveling grate stoker, capacity 185,000 lbs. of steam per hour, pressure 1,425 lbs., steam temperature 930° F.; VU steam generator, C-E pulverized fuel system, capacity 70,000 lbs. of steam per hour, pressure 450 lbs., steam temperature 605° F.; premier boiler with Skelly stoker, capacity 1000 lbs. per hour. (From a list from Combustion Engineering Company, Inc., 200 Madison Avenue, New York.)

salts accumulate, and such solutions cause "priming" and other difficulties. By opening the blow-off cock, shown in Figure 91, a portion of the contents is removed and replaced by cleaner water. The task of supplying clean water to the boiler is lightened by returning all clean condensed steam to the boiler room. The boiler feed water is generally preheated.

Recent work in the Bureau of Mines has led to the recommendation that trisodium phosphate be used for conditioning boiler water. The muds formed are more soluble, or as soluble, in very hot water and therefore do not form a scale, but float so that they can be removed by a special filtering installation. It has been shown in the course of this work that soda ash solutions tend to render steel brittle. Calgon and Buromin are such sodium phosphates especially developed for water conditioning.

Carbonate hardness may also be removed by heating in a vessel with trays, having provision for the escape of the carbon dioxide driven out. The calcium carbonate precipitates on the trays, which are removed and cleaned periodically. Non-carbonate hardness is not removable by this method.

Another way to soften water is to pass it, cold, over zeolites,[23] as described in the next chapter, where the subject of water softening is presented in more detail.

Mechanical Stokers. Hand shoveling of coal is still practiced, and in smaller plants has much in its favor. In larger plants, mechanical stokers are used in order to save labor, and also to prevent smoke and to give a more uniform fire. The Taylor stoker has an inclined stationary grate; each "retort" has two rams or plungers, one above the other, and a number of retorts make up the stoker. Between the retorts a step-like surface is provided, with holes at each step through which the forced draft enters the fire. The upper ram moves fresh coal under the blanket of fire, so that the heat causes the volatile portions to pass out and over the bright fire where they are consumed, thus preventing smoke. The lower ram pushes the bed of coal outward and downward toward the dumping platform. The motion of each ram is slight, only a few inches, and the strokes are 1 in 2 minutes (adjustable). The Taylor stoker belongs to the class of underfeed stokers.

There are a number of multiple retort underfeed stokers on the market, such as those manufactured by Westinghouse Electric Company and Combustion Engineering Company. An interesting and popular stoker is the spreader stoker, an overfeed type which distributes the coal from a point one or two feet above the grate at the front of the furnace by either mechanical or pneumatic means. Still another mechanical stoker is the chain grate, consisting of an endless belt as wide as the fireplace, moving very slowly toward the rear of the boiler. Fresh coal is fed by gravity to one end of the grate which carries it into the hot zone; at the turn, the ashes are dumped. The chain grate stoker operates either with natural draft or with forced draft.

A flue gas analysis indicates whether or not proper burning is taking place; no carbon monoxide should pass out as such, but should be burned to

[23] *Ind. Eng. Chem.*, 19, 445 (1927).

carbon dioxide. The excess of air should be small. Such analyses are made by means of the Orsat apparatus, carrying a measuring bulb and absorption pipettes.[24] This control is used constantly, but is more important with hand firing than with mechanical stokers. The temperature of the stack gases is 500° to 600° F. (260° to 315° C.).[25] If the load on the boilers is not steady, that is, if steam is drawn off irregularly, it is important to alter the intensity of the fire by altering the draft; in case of hand firing, with natural draft, a Locke damper regulator is a simple equipment which responds quickly. Automatic carbon dioxide recorders are on the market.[26]

Even mechanical stokers are now regarded as developments of a past age; the most modern method of applying coal energy to the boiler is by means of powdered coal. A heavy-duty pulverizer is set close to the boiler, and is swept by a blast of air which carries the fine coal (through 200 mesh) into the burner, where it burns like gas or oil. A melted slag accumulates in the bottom of the boiler setting, and this is drawn off by tapping just as a blast furnace is tapped. The coal must be bituminous.

Hydroelectric Power

The utilization of water power to its full capacity is a modern development which had to wait until the science of generating electric current was sufficiently advanced. By means of the electric current, the enormous quantity of power developed in one spot, at a waterfall, for instance, may be distributed over a wide area many miles away. If water power had to be used as mechanical power (rope and belt drives), the present-day developments would not exist. Hydroelectric power is important because it is independent of a supply of coal. The cost of installation of a hydroelectric power plant may be greater than that of a steam power plant, but the running cost is lower. (See also p. 241.)

Water power is transformed into electrical power by applying the water to a wheel (turbine), which carries on the same shaft the pole pieces, for example, of an alternating-current generator; the armature is stationary. The opposite arrangement is used less often. At Niagara Falls, the voltage is 12,000; for distance transmission, this current is raised to 60,000 volts in oil transformers. Direct current is produced from the alternating current by applying it in the separate manufacturing plants to the motor of a direct-current generator. Water power may also be transformed directly to direct current.

The penstock brings the water from the upper level to the level at which the waterwheel is situated, and delivers it to a spiral casing surrounding the wheel. It enters the buckets of the wheel and escapes downward, best through a draft tube in which suction is developed which acts on the wheel by decreasing what might be called the back pressure. In the latest plant

[24] There are 3 absorption pipettes: *a* alkali solution for CO_2; *b* alkaline pyrogallol for oxygen; *c* ammoniacal cuprous chloride for CO.

[25] For a complete heat balance sheet, see Marks, "Mechanical Engineers' Handbook," New York, McGraw-Hill Book Co., 1941, p. 1165.

[26] For example, the Ranarex, described in Chapter 46.

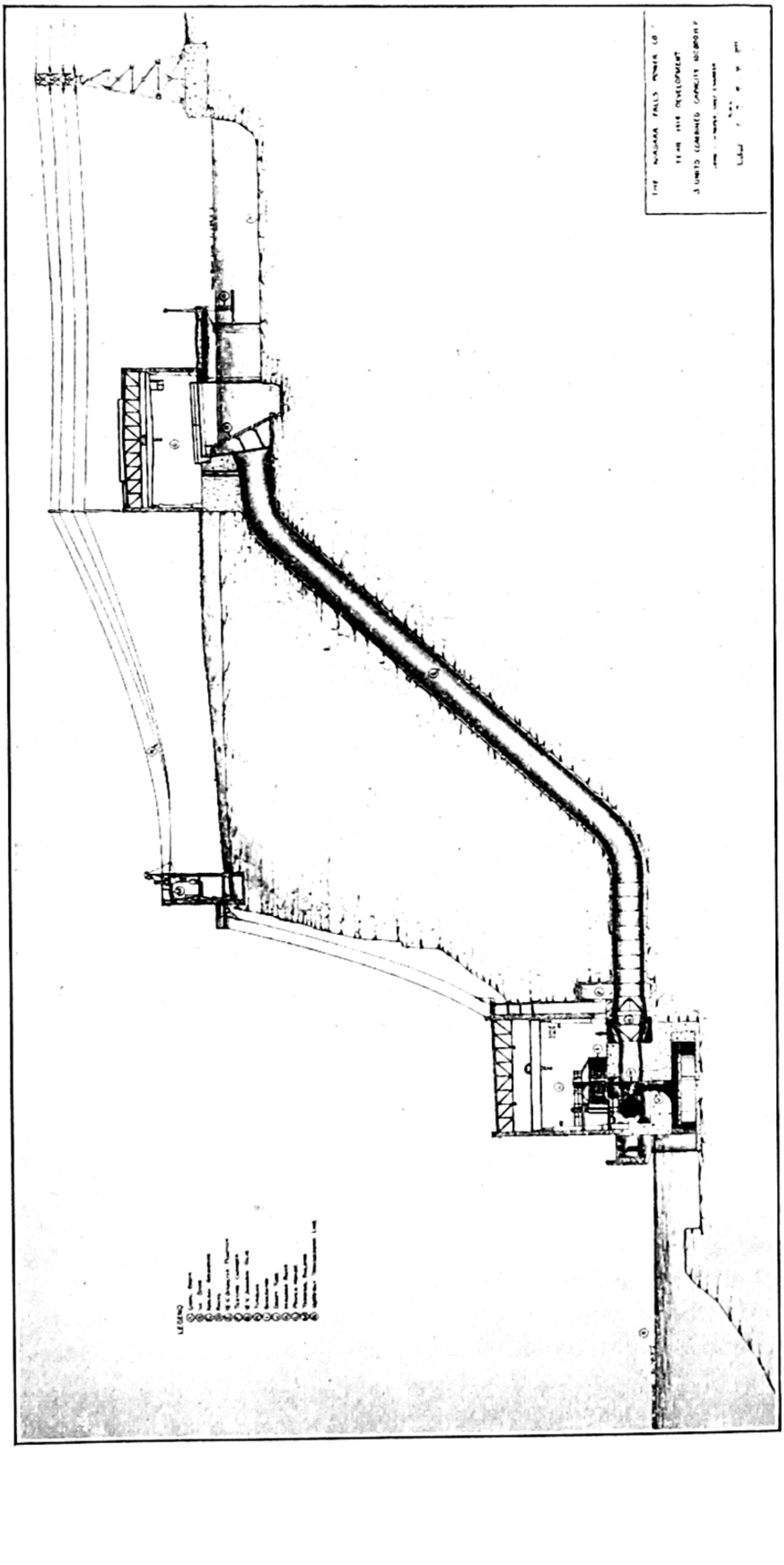


FIGURE 92.—The application of water to a turbine wheel; cross-section through the forebay and terminal basin of the hydraulic canal and tunnel, penstock cut in the rock, Johnson regulating valve, draft tube for escaping water, and generator. Niagara Falls Power Company Plant 3B, in the gorge. The difference in levels averages 217 feet. (By permission.)

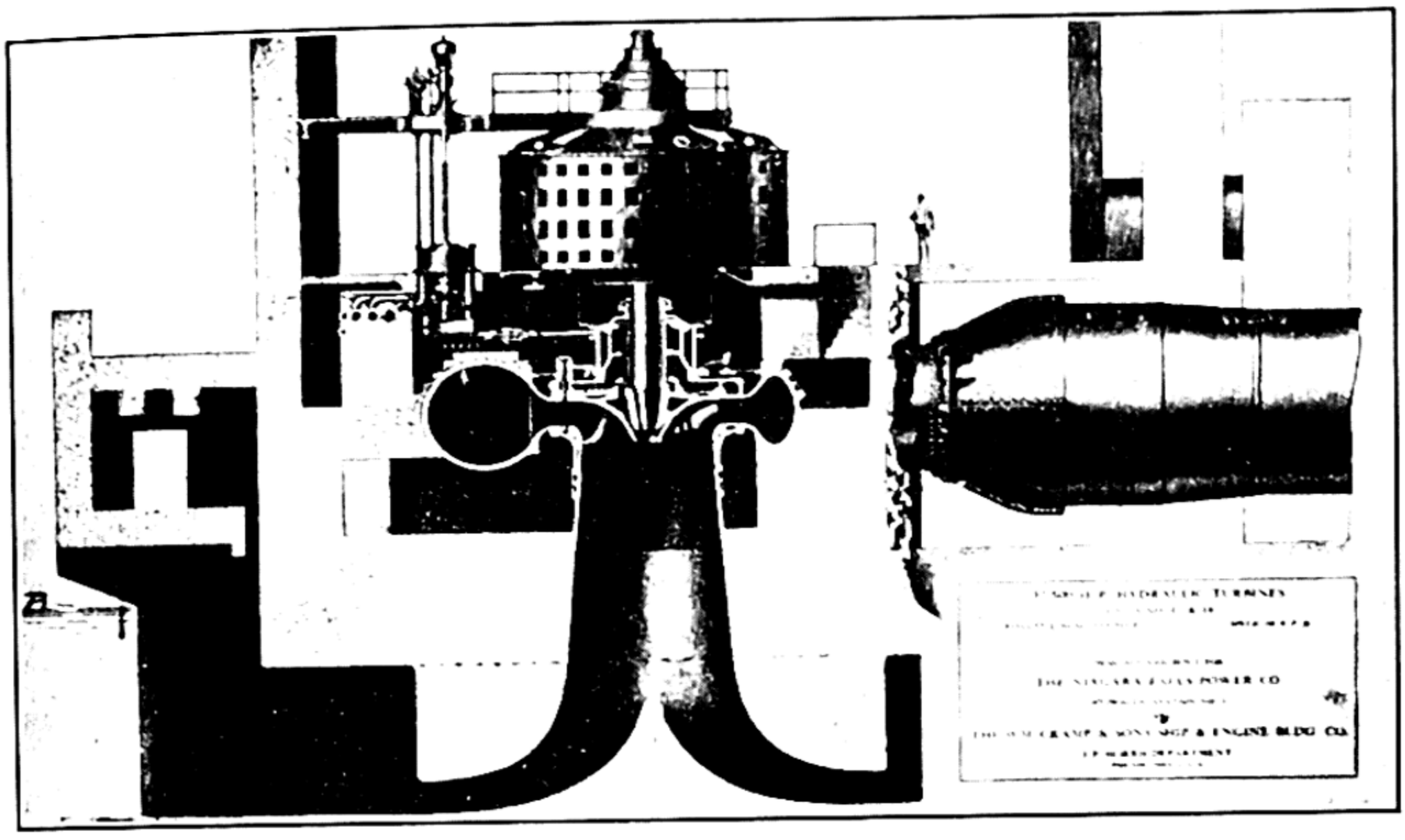


FIGURE 93.—Assembly of generator, water wheel and casing, and draft tube for the escaping water. The water from the penstock, at right, reaches the casing in the wider part first. Mean level of river shown at *R*. Niagara Falls Power Company Plant 3B. (By permission.)

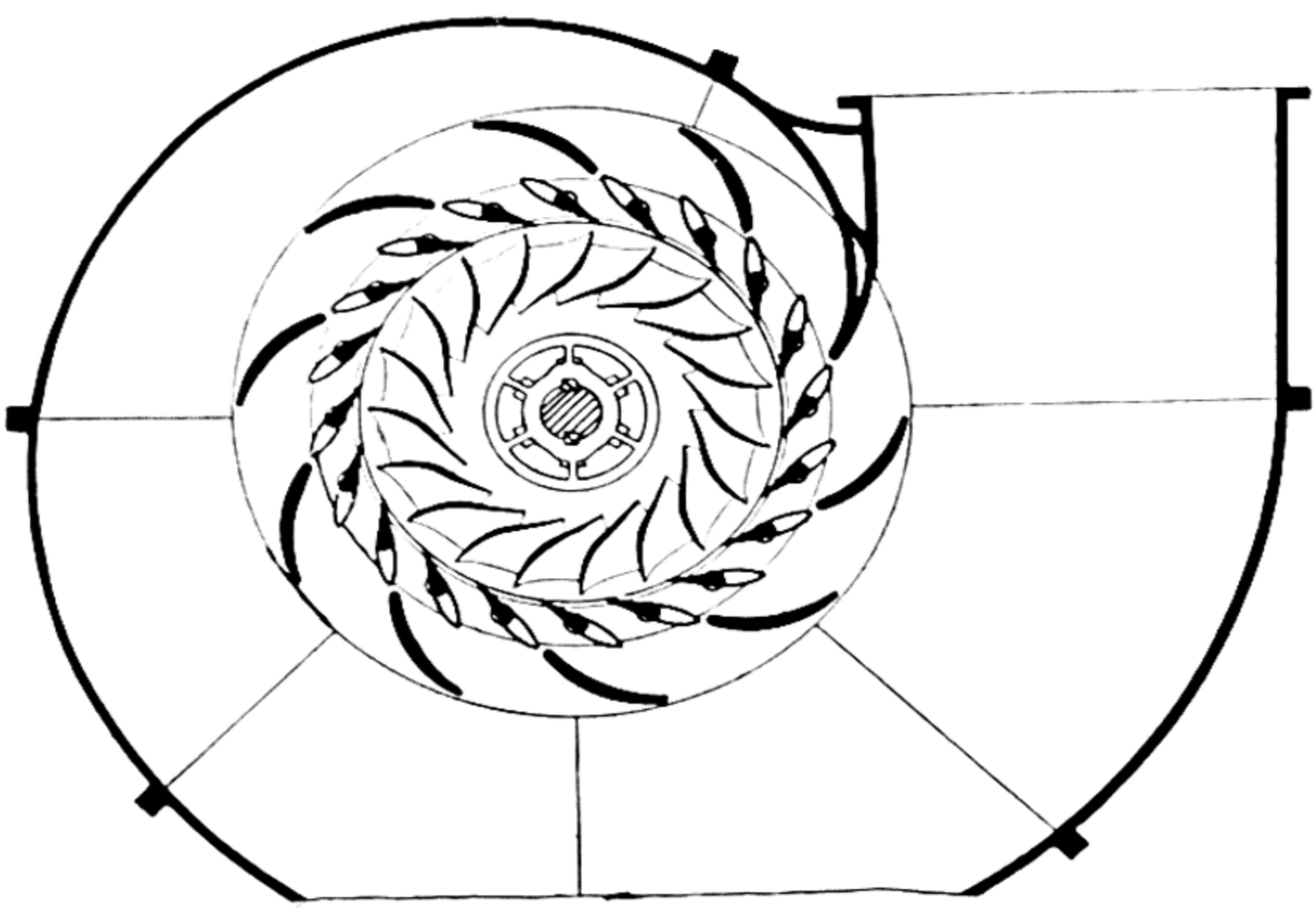


FIGURE 94.—Horizontal cross-section through water wheel, wicket gates, guide vanes, and casing. The water wheel is 16 feet in diameter, and its speed is 107 r.p.m. The water escapes downward. Niagara Falls Power Company Plant 3B. (By permission.)

at Niagara Falls, the penstock is cut into the solid rock, lined with concrete (*see* Figure 92). The second illustration (Figure 93) indicates the relative location of penstock, casing, water wheel and generator; the third (Figure 94) gives details of the casing and water wheel. The generator shown develops 37,500 horsepower or 28,000 kilowatts (27,964). Hydrogenerators are built as large as 70,000 or more horsepower.

The capacities for the major hydroelectric power projects are shown in Table 40.

TABLE 40.—*Capacities for the major hydroelectric power projects in kilowatts. (Estimated, June, 1937, unless otherwise stated.)*

	Present installed capacity	Ultimate installed firm power
Niagara river, at Niagara Falls	986,000 (Can.) 561,000 (N. Y.)	
Boulder Dam, Colorado river, 1942	869,800	1,000,000
Grande Coulée, Columbia river, 1942	344,000	2,520,000
Bonneville, Columbia river[22b]	86,400	688,000
Wilson Dam, Tennessee river	261,400	620,000
Norris Dam, Clinch river	132,000	235,000
Pickwick Landing Dam, Tennessee river	96,000	288,000
Wheeler Dam, Tennessee river	90,000	612,000
Chickamauga, Tennessee river	72,000†	210,000
Guntersville Dam, Tennessee river	68,000‡	134,000
Conowingo, Susquehanna river	378,000	594,000
Total potential capacity for the United States*		80,000,000
Total installed capacity, U. S.*	20,000,000§	

The flow of the water over the year is steady for the Niagara River, fairly steady for the Colorado and Columbia Rivers; it fluctuates widely for the Tennessee and Susquehanna Rivers. In installed capacities, the states rank as follows* for 1936: California, 15.2 per cent of total; New York, 11.7; Washington, 6.4; North Carolina, 6.1; Alabama, 5.4; South Carolina, 5.; Maine, 3.8; New Hampshire, 3.6; Pennsylvania, 3.5; Georgia, 3.5.

* Geological Survey, January 6, 1936.
† To be completed in 1939.
‡ To be completed in 1938.
§ The installed water power in the United States on January 1st, 1941, is given as 18,868,027 horsepower, equivalent to 14,072,500 kilowatts, by the Federal Power Commission. In 1938 there were two 43,200 kilowatt generators in operation at Bonneville (quoted from [32]).

STEAM-GENERATED POWER

Steam is not usually generated from electric current, but a practical method for such generation has been described.[27] The opposite process, however, the generation of electric power from steam, is a universal one. A steam plant may be installed at lower first cost than a hydroelectric power plant, under ordinary conditions; it may be installed at any point to which coal may be hauled, and where there is an adequate supply of condensing water; it has the third advantage of being flexible, that is, its output may be reduced for any period of time, even for periods of an hour or less, with a corresponding reduction in coal. Hydroelectric power, on the other hand, cannot be shut down economically, for the raw material—the flowing water—passes at the same rate throughout the 24 hours. In the Buffalo

[27] "The Electric Steam Generator," an article by Horace Drever, *Ind. Eng. Chem.*, 14, 923 (1922).

District, the hydroelectric plants carry a base load that is, a load which is constant over the 24 hours of every day. A certain portion of the base load and all the peak loads are carried by a large steam plant of 622,000 h.p. By this combination, the most efficient use of both sources of power is made.

The modern method for generating electric power from steam is to produce the steam at high temperature and pressure from highly efficient,

FIGURE 95.—Aerial view of Grande Coulée dam.

pulverized-coal burning boilers and to apply this to a steam turbine with a horizontal shaft which is direct-connected to the field of an alternating-current generator. For example, the newest generating unit of a large steam station [28] has a 17-stage turbine. Each stage consists of a turbine wheel with numerous stainless steel ("Ascoloy") buckets varying in length from 3 inches at stage 1 to 20 inches at the last stage, and also varying in width from ½ inch to 2 inches or more. The buckets are set radially near the periphery, and a stationary piece, called the diaphragm, is mounted close to it; the diaphragm has similar curved buckets, set in the opposite sense, which act as guides for the steam and send it into the curve of the rotating buckets just next to it. The speed is 1800 rpm, and the capacity of the generator is 80,000 kilowatts; the voltage is 12,000. Single-shaft generators are built with capacities varying from 20,000 to 80,000 kilowatts. The

[28] Buffalo Niagara Electric Corp. Steam Plant, Huntley Station.

steam is generated in one boiler, which produces 900,000 lbs. of steam per hour, at 1500 lbs. pressure, and at a temperature of 900° F. At the turbine throttle, the pressure is about 1250 lbs., and the pressure drops in the successive stages until it leaves the last one at ½ to 1 inch of mercury back pressure.

The unit just described is a condensing unit, which means that the last stage delivers to a surface condenser. The amount of condensing water necessary is considerable, amounting to approximately 60 gallons of water per hour for each kilowatt of capacity. There are also *topping turbines* which deliver at the last stage a stream of steam at an appreciable pressure, and work, for example, from a high of 1500 lbs. to a low of 250 lbs. without condenser. The 250-lb. steam may be used in various ways; in a power station it may be needed for application to suitable turbines, generally of older design, which themselves are condensing units.

The boiler and turbine combination here described will produce a kilowatt hour of electrical energy with 0.83 lb. of coal.

The average efficiency in the electric public utility power plants is indicated by the figure of 1.3 pounds of coal per kilowatt-hour generated, for 1946, which is the same figure as for 1945, and which contrasts with 3.2 pounds in 1919.[29]

Linked with consideration of fuel economy are the Kleinschmidt compression stills, thousands of which supplied naval vessels with pure water made from sea water. The Kleinschmidt compression still is remarkable for its high fuel economy, achieved mainly by mechanically compressing the steam, thereby raising its temperature (by 9° F.). The compressed steam can then evaporate the sea water, furnishing further amounts of steam to be compressed and condensed. A brine concentrate is constantly wasted, but its heat as well as that of the condensed steam, the fresh water, is retained in the system by a three-way heat exchanger. The Kleinschmidt still averaged 175 pounds of distillate for each pound of fuel consumed.[30]

A few more words regarding the 900,000-lb. per hour boiler described above may be of interest, and will complete the picture. (*See* Figure 96.) The boiler is better named a water-cooled furnace, or rather, a two-stage water-cooled furnace. The fuel is pulverized coal, crushed and ground close to the furnace, to minus 200 mesh, and swept into the primary furnace by a stream of preheated (moderately) primary air, the velocity of which is so adjusted that the flame forms about 1 to 2 inches away from the burner tip. The primary furnace is lined with studded tubes, covered with a plastic refractory, chromeore. In the secondary furnace, part of the tubes at least may be of the block type; these are the longest tubes. The water is distilled, but nevertheless there is a softening treatment, and also an oxygen-destroying treatment with sodium sulfite. The blowdown is continuous. The furnace has a superheater, which in this construction is of the draining type, an economizer, and an air heater in the flue gas which furnishes 500° F.

[29] Bureau of Mines, Coal Economics Division.

[30] "Compression distillation," Allen Latham, Jr., Arthur D. Little Inc., Cambridge, Mass., a paper presented at the November meeting, 1945, of the American Society of Mechanical Engineers.

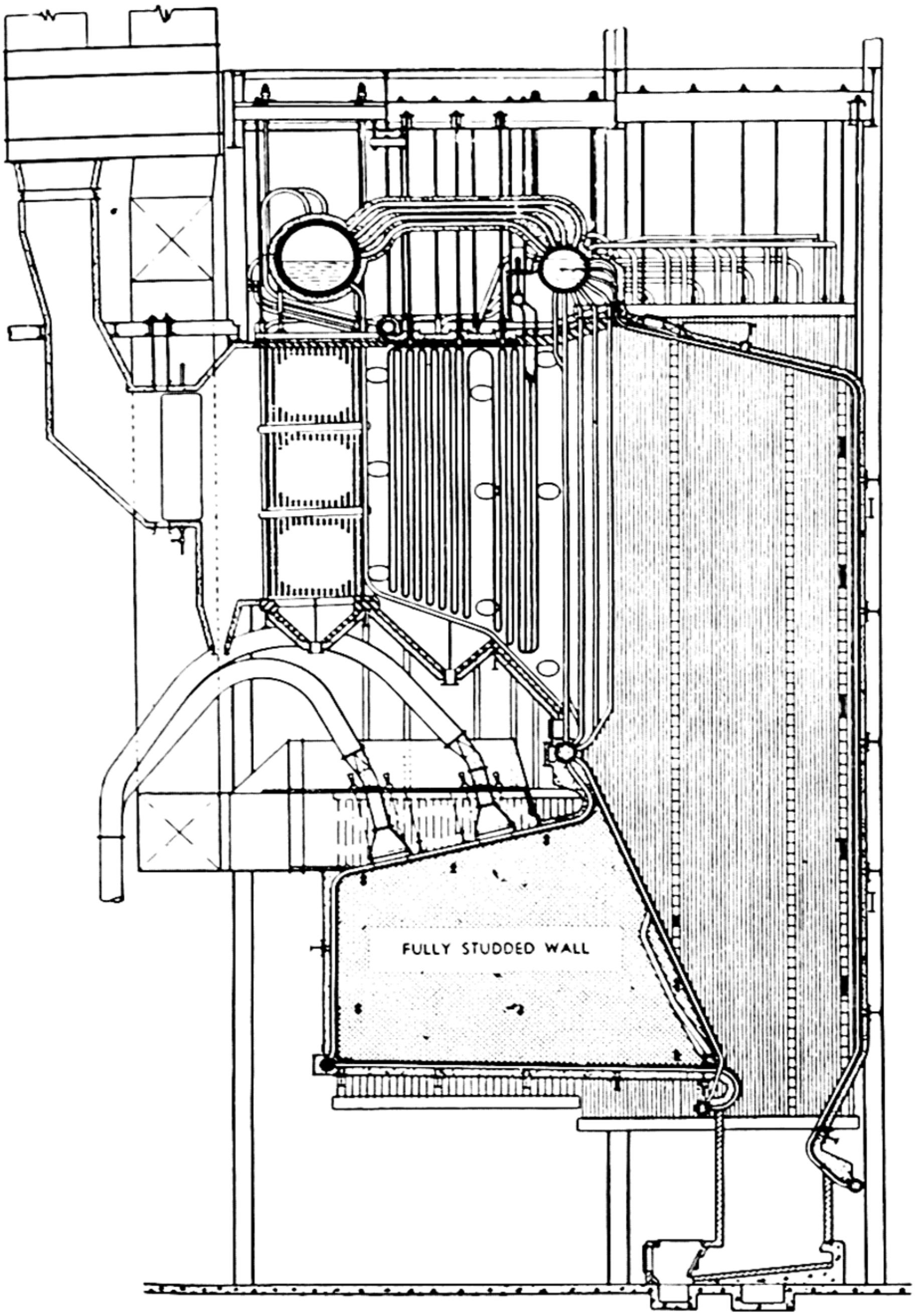


FIGURE 96.—A two-stage water-cooled furnace, of the slag-tap type. The primary furnace has stud-tubes for its walls; the secondary has block tubes. The conventional boiler heating surface is largely eliminated. The fuel is pulverized coal, applied through the large diameter, curved tubes in middle left, as shown. This unit develops 605,000 pounds of steam per hour at 1475 pounds pressure and 950° F. total temperature. Note the superheater, below and between the drums; the three sections of the economizer to the left of superheater, and the air heating unit to the left and above the main drum. (Bulletin G-16, p. 24, "Water-cooled Furnaces," The Babcock and Wilcox Company, 1515 Guardian Building, Cleveland, Ohio.)

secondary air. The ash in the form of slag is tapped periodically, as already suggested in a previous paragraph, but here the hot slag strikes a water table (made up of high-velocity jets of water) and is disintegrated, so that it can be pumped away in granulated form. A 66″ drum at the top of the boiler acts as a storage reservoir for the water in the boiler. If the steam output of this large boiler were to decrease suddenly, the pressure would suddenly increase. The increase in pressure would decrease the volume of the steam bubbles which are constantly being produced in the water walls of the boiler. The reservoir action of the drum instantly supplies water to the boiler tubes to take up the space made as a result of the collapsing steam bubbles. If this water was not supplied instantly, serious damage might result from overheated tubes. Another purpose of the drum is to provide a means of separating the steam from the water. For most efficient operation, the steam leaving the drum should contain as little water as possible. The drum contains "scrubbers" and "cyclone separators," enabling it to deliver dry and clean steam to the superheater. Two large pipes (30 inches) carry water from the upper drum to the lower headers feeding the long vertical tubes; the circulation of the water is down these two pipes, and up the long tubes to the upper drums. The over-all height of the boiler is that of a five-story building. An elaborate instrument board gives all vital information instantly.

Mercury vapor has been used as the working substance in a boiler and turbine for several years, and on the experience gained thereby, three new improved *mercury vapor systems* have been installed at Hartford, Conn., Kearny, N. J., and an outdoor station at Schenectady.

In the original 1928 installation, an over-all thermal efficiency of 33 per cent was obtained through the year. In the new ones, it is expected that 36 per cent will be reached. In a porcupine boiler, with cylindrical finger-like extensions on its lower part, and preheated, mercury is vaporized by direct heat from an oil burner or pulverized coal burner; a temperature of 885° C. (1625° F.), under a pressure equivalent to a column of liquid mercury 17 feet high, is recorded. The mercury vapor drives a turbine; the exhaust vapors pass to a steam boiler, in which 400 lbs. of steam is raised. The steam is superheated and drives a turbine also.

The cost of *steam-generated electrical power* depends upon a number of factors, one of which is the cost of coal. Coal at the mine in 1946 was priced at $3.44 per long ton. To this must be added the cost of freight which, to many large centers, equals and even surpasses the mine cost. For this reason, steam plants situated at the mines, and called *mine-mouth plants*, have a great advantage, especially if the power is used on the spot or close by; for if the current must be transported, a cost of transmission appears which takes away some of the merit of such a station. The cost of transmission over a distance of 200 miles is computed as 2.62 mills per kilowatt-hour; over 100 miles it is 1.92 and over 50 miles 1.65. Mine-mouth plants are comparatively rare, partly because a second requirement is an abundance of cooling water, and this is not often fulfilled; rather is it more common to find that steam power plants are almost always located

where there are large and cheap supplies of condensing water, for it is much cheaper to haul coal to the plant than to transport water.

Prices for electrical power vary in different localities; for industrial users, firm power on contract at $18 a horsepower year was considered fair a few years ago. Firm power means a stated number of kilowatts at all times; there is no opportunity to vary as a householder does who buys on the meter. Eighteen dollars per horsepower year is equivalent to 2.75 mills per kilowatt hour. It is said that the Rjuken development in Norway, part of the Norsk Hydro, using water from a natural lake at the head of a river which drops 2000 feet in a short distance and sending the water through two power-houses a few miles apart, develops power for $3.00 per horsepower year.[31] This is probably the most favorable figure in the world. By moving into isolated places with favorable conditions of head and volume of water, and with no requirement of dam building, a cost of $10 to $15 per horsepower year may be achieved. The large government plants will and do already furnish frm power for similarly low figures. Power at Bonneville, for which rates have been approved by the Federal Power Commission, will be obtainable as firm power for $14.50 per kilowatt year, equivalent to $10.81 for the horsepower year. The rates at Boulder Dam, up to May 31, 1942, were 1.163 mills per kilowatt hour for firm power, equivalent to $10.19 per kilowatt year, measured at the power plant; secondary energy 0.34 mill per kilowatt hour.

The *cost of steam-generated power* depends upon the cost of coal, as already mentioned, upon the fuel efficiency, for which figures have been given, upon the installation cost per unit of power, upon the load factor and other factors. As to the investment cost, it was estimated in 1937 that the initial investment for a steam plant is $83 per kilowatt hour to be produced, and for a hydroelectric plant $250 per kilowatt. As to the latter figure, the estimate of $126 per kilowatt is made in a study by the Power Authority of the State of New York; as to the former figure, the Authority computes that $93 per kilowatt of installed capacity is as low a figure as can be taken (1937).

In comparing hydroelectric power with steam power, it is unwise to generalize, because installations differ, especially in favorable and unfavorable factors.[32]

[31] *Ind. Eng. Chem.*, 28, 146 (1936).

[32] "Government Hydro Versus Private Steam Power," a study in relative economy, prepared by the Power Authority of the State of New York and submitted to the President on November 22, 1937. This study provides the only published report on the relative economy of hydroelectric power and steam power; it embodies figures submitted by a private consulting engineer, Mr. F. F. Fowle, Dean of Engineering at Purdue University, and also criticisms and corrections by the members of the technical staff of the Power Authority of the State of New York. The original figures of Mr. Fowle showed 4 mills per kilowatt hour as the cost for steam power, and 6.3 mills for hydroelectric power. The Authority representatives alter the figures after a number of considerations, so that the steam power figure reads 6.3 mills, while the hydroelectric power figure reads 2.1 mills. According to Mr. Fowle, steam power is cheaper, 4 mills versus 6 mills, while according to the Authority representatives, hydroelectric power is cheaper by much more, 2.1 mills against 6.3 mills. The reader is referred to the study for additional data.

Cold Production or Refrigeration

Temperatures just above the ice point, and below, are reached chiefly with the aid of chemical refrigerants. Arranged in the order of their importance, the substances used are anhydrous ammonia, carbon dioxide, sulfur dioxide, dichlorodifluoromethane ("Freon-12"),[33] methyl chloride, methylene chloride, ethyl chloride, and paraffin hydrocarbons. Ammonia is by far the most commonly employed refrigerating agent; it is used for ice manufacture; for cold storage of meats, fruits, vegetables and dairy products, and for general refrigeration.[34] Carbon dioxide is a somewhat less efficient agent; it is used instead of ammonia when the odor of the latter in case of leak would be objectionable, for instance in hotels, in some hospitals, and on board ship. It and "Freon-12" are used also for temperatures below those which ammonia can furnish. Sulfur dioxide is the most generally used "working substances" for household refrigerators; for the same purpose, but less generally, methyl chloride is utilized. Paraffin hydrocarbons, *i.e.*, ethane, propane, butane, and isobutane, are used only in special cases. With any of the agents listed, the method consists of compressing the gas sufficiently so that on cooling with ordinary cooling water, it will liquefy, and then sending the liquid, still under pressure, to an expansion valve leading to coils in which the expansion takes place; heat is abstracted from the surrounding liquid or room, to make the expansion of the liquid to gas possible. The expanded gas is compressed, and sent through the system again. The same material serves over and over; only the losses due to leaks must be replaced.

The "Servel" and "Electrolux" refrigerators run on a gas or other flame, using as working substance aqua ammonia.[35]

The boiling points at atmospheric pressure for the various working substances follow:[36]

Ethyl chloride C_2H_5Cl	+ 55° F.	or +12.5° C.
Sulfur dioxide SO_2	+ 14	or −10
Methyl chloride CH_3Cl	− 11	or −23.9
Dichloro-difluoromethane, CCl_2F_2	− 21.6	or −29.8
Anhydrous ammonia NH_3	− 28	or −33.3
Propane C_3H_8	− 49	or −45
Carbon dioxide CO_2	−108.8	or −78.2

For an ammonia system, cast iron, wrought iron, and steel are used; copper and brass are avoided. The essential parts for a refrigerating plant using brine as an intermediate cooling substance are shown in Figure 97. The pressures are moderate; on the high-pressure side, the gas is compressed to 155 lbs., with a temperature of 210° F. (99° C.). The gas is cooled to 75° F. (24° C.), with the pressure maintained near 155; it liquefies and

[33] "Freon-11" is trichlorfluoromethane; "Freon-22" is difluoromonochloromethane.

[34] Wax is separated from oil by ammonia refrigeration (Chapter 24); for the liquefaction of chlorine, either ammonia or carbon dioxide may be used (Chapter 5).

[35] See "Chemical Machinery," by E. R. Riegel, p. 469, New York, Reinhold Publishing Corp., 1942.

[36] For explosion limits and physical properties other than boiling point consult "Properties of Refrigerants," Circular 2, 1926, American Society of Refrigerating Engineers, 37 West Thirty-ninth Street, New York.

collects in a receiver. A small stream is sent through the expansion valve (an ordinary iron globe valve) to the low-pressure coils, where the liquid turns to gas, absorbing heat from the brine. The brine is circulated through a suitable system of pipes (pump). A temperature of 15° F. (−9.4° C.) for the brine is usually reached. The gas returns to the compressor with a pressure of about 20 lbs.

The sources of ammonia are discussed in Chapters 6 and 14.

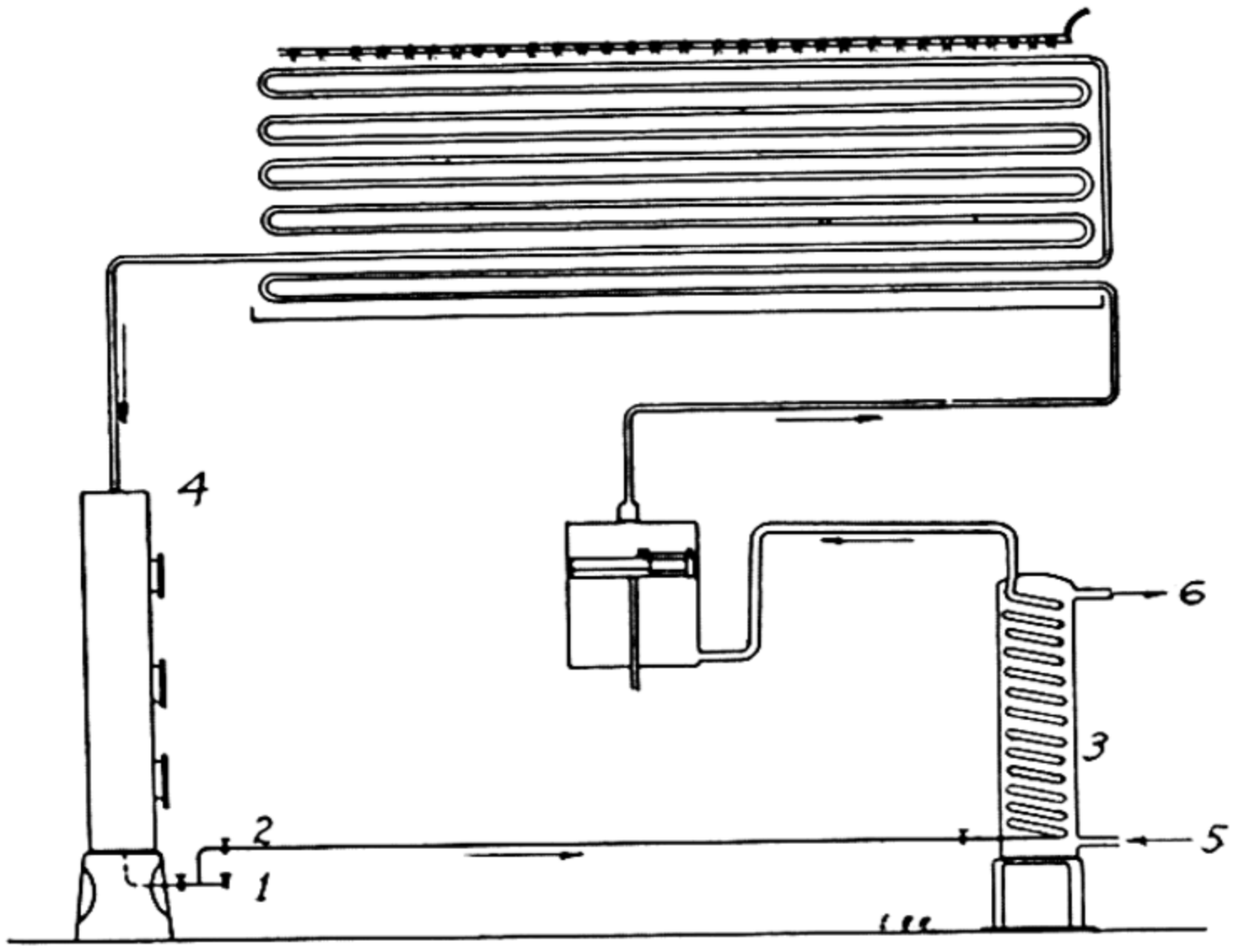


FIGURE 97.—Refrigerating plant with ammonia as working substance. Fresh supplies from purchased cylinders are introduced at 1 into the receiver 4; the liquid enters the cooler, vaporizes, and reaches the compressor and condenser. The liquefied ammonia collects in receiver 4 and is used over again. The brine enters the cooler 3 at 5, and leaves at 6; brine circulation not shown.

In the liquid carbon dioxide refrigerating system, the pressure on the high-pressure side (condenser) is 1000 lbs.; on the low-pressure side (expansion coils) 300 lbs. per square inch. The condenser temperature must be as much below 88° F. (31.1° C.), the critical temperature,[37] as possible.

CARBON DIOXIDE

Sources

Carbon dioxide is used commercially as a gas (soda ash manufacture), compressed as a liquid in steel cylinders (soda fountains, for refrigeration, and as convenient source of the gas), and as the solid. It is obtained from (1) the combustion of coke; (2) the calcination of limestone; (3) as a by-product in syntheses involving carbon monoxide; (4) as a by-product in fermentations; (5) by the action of sulfuric acid on dolomite; (6) from

[37] The critical temperature is the temperature above which the gas cannot be liquefied, no matter how great the pressure; *see also* footnote 31.

wells.[37] Gas from any one of these sources may be made into the gaseous, liquid, or solid form of carbon dioxide.

The utilization of the carbon dioxide in the combustion gases of coke involves the alternate formation and decomposition of alkali bicarbonates in solution. Hard coke is burned under boilers, and the fuel gases are so regulated that a maximum content of carbon dioxide, 16 to 17 per cent, is obtained. The gases enter a scrubber (tower) packed with limestone to remove sulfur compounds and fed with water to cool the gas and arrest the dust. The cold gases enter the absorber, a tower packed with coke down which a solution of potassium carbonate passes; carbon dioxide is absorbed, and the saturated solution is run to a boiler where the absorbed gas is lib-

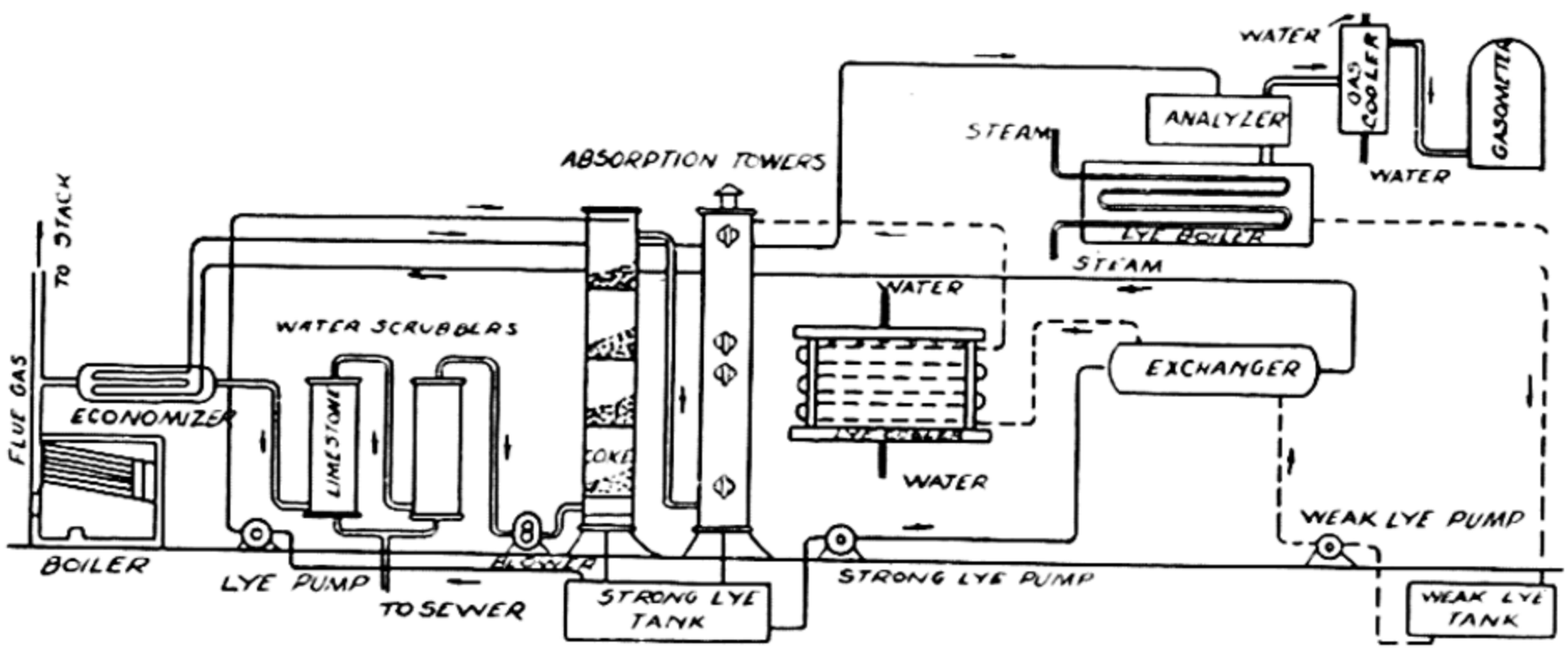


FIGURE 98.—Diagrammatic flow-sheet for the absorption of carbon dioxide in the fire gases from burning coke. The gas dissolves in a strong lye solution, from which it is driven out by heat, giving 100% CO_2 gas. (Courtesy of the Frick Company, Waynesboro, Pa.)

erated by heat. It is under this boiler that the coke is burned. The operation is continuous; charged solution flows in constantly, while the spent liquor is run off constantly. By means of an interchanger, the outgoing liquor heats the incoming liquor to some extent. The outgoing liquor, cold, returns to the absorber. The gas from the boiler is very pure. It is dried in a calcium chloride tower, and compressed to 100 atmospheres, at which pressure it liquefies at ordinary temperatures. (*See* Figure 98.)

The other sources are presented in their proper places, except source (5), which is unusual. In Georgia,[38] a deposit of dolomite is mined, and the crushed rock treated with sulfuric acid in carbonators provided with a cover and gas outlet. The residue in the carbonators is a solution of magnesium sulfate, in which calcium sulfate is suspended. By keeping the solution on the acid side, no detectable quantity of calcium salt dissolves. The solution is made into Epsom salts, $MgSO_4 \cdot 7H_2O$, a laxative, and a material which serves in the leather industry. The carbon dioxide is compressed to the liquid and used in the preparation of carbonated beverages.

[37] "Solid carbon dioxide from Mexico," James Welford Martin, *Ind. Eng. Chem.*, 23, 256 (1931).

[38] "Manufacture of carbon dioxide and Epsom salts," W. P. Heath, *Ind. Eng. Chem.*, 22, 437 (1930).

In addition to the uses which have been mentioned, carbon dioxide serves as a chemical in the manufacture of salicylic acid, white lead, and other products, as well as in fire fighting devices of various kinds. Fire extinguishers of the wall type, also called the soda-acid type, contain 2½ gallons of saturated sodium bicarbonate solution and 4 ounces of concentrated sulfuric acid in a small bottle. On inversion, the acid reaches the solution and liberates carbon dioxide; the pressure developed expels the liquid through a nozzle to a distance of 30 to 40 feet. The main extinguishing agent is the water. Liquid carbon dioxide under pressure in steel cylinders may be released so that a carbon dioxide snow forms which may be directed into the gaseous blanket over the fire. The "firefoam" extinguisher system relies upon the smothering action of a foam blanket produced by the interaction of a sodium bicarbonate solution with an alum solution, in the presence of a foam stabilizer.

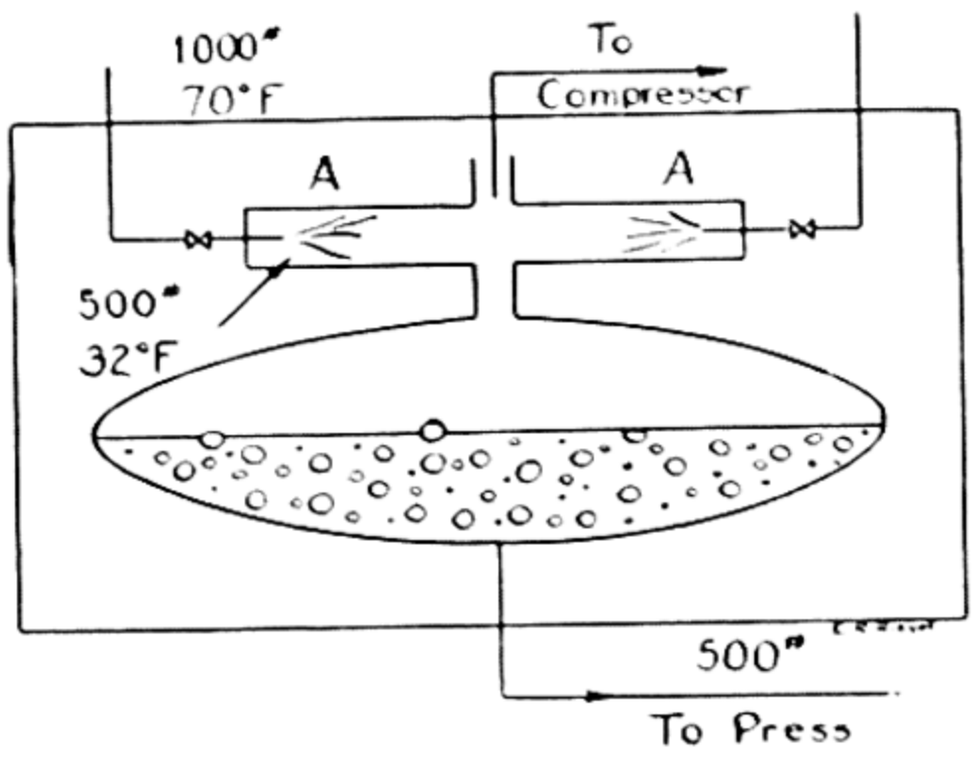


FIGURE 99.—The "evaporator," in which the liquid carbon dioxide is formed and stored.

Solid carbon dioxide is obtainable in commercial quantities. It is supplied in block form resembling the familiar artificial ice cake. Its uses are similar to the uses of ice, but it functions without melting, and without producing drips; it vaporizes, and leaves only a gas, which may be easily vented, so that it has received the rather apt name of "Dry Ice." Its manufacture will be described for the case of a plant particularly well situated with regard to its source of raw material.[39].

Pure, liquid carbon dioxide under a pressure of 1000 pounds and at a temperature of 70° F. (21° C.), is delivered to the plant by a pipe system. It is sent to the "evaporator" (Figure 99), where its pressure is reduced to 500 pounds, with a simultaneous drop in temperature to 32° F. (0° C.). With the pressure set at 500 pounds, the liquid maintains itself at that temperature; as this is lower by several degrees than the room temperature, heat flows in and causes the liquid to simmer quietly. About 25% of it boils away. The vaporized portion is sent to a special compressor which delivers it as gas to the main compressor gas line, at a pressure of 1000 lbs.

The 32° F. liquid from the evaporator is admitted to the press chambers (Figure 100); these have movable tops and bottoms, worked by hydraulic pressure. The chamber is 20 by 20 inches, and 24 to 30 inches deep. The

[39] The Dry Ice Corporation's plant at Niagara Falls, N. Y.

liquid enters through an ordinary nozzle; part of it expands to gas, and draws its heat largely from the incoming liquid, which is thus solidified to a fluffy snow. The gas formed is drawn off constantly by the suction line of the main compressors and recompressed. By operating the top and bottom walls, the snow is compacted to a solid block 20 by 20 by 10 inches. Each press makes 6 to 8 cakes per hour. The density of the resulting cake is controlled by the amount of snow pressed into the 10-inch space. After

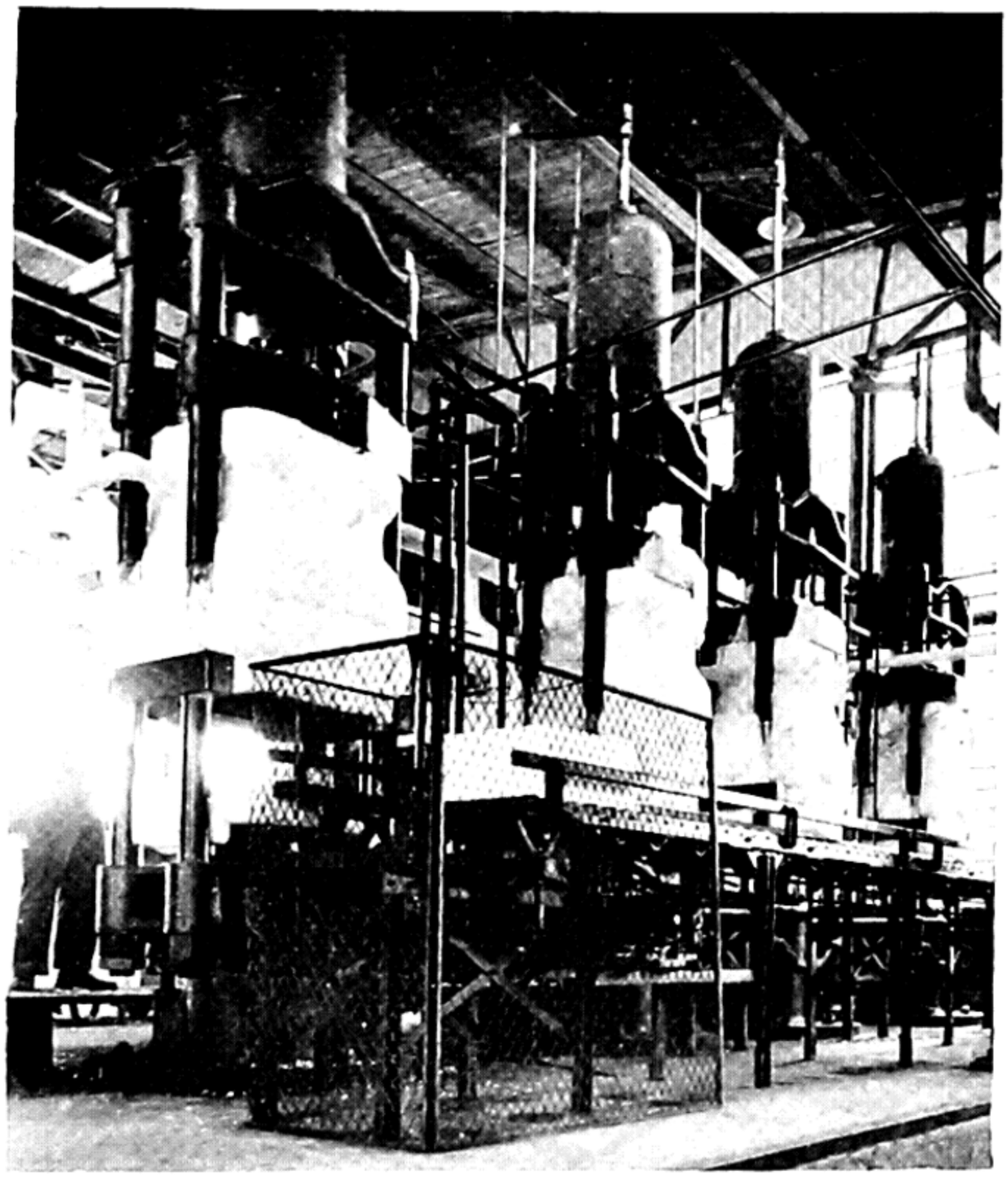


FIGURE 100.—Press chambers, in which the carbon dioxide snow is pressed into blocks; one of the blocks may be seen on the conveyor. (Courtesy of the Dry Ice Corporation of America, New York.)

discharge to a conveyor, the block reaches band saws, which cut it into four smaller blocks, each a 10-inch cube, weighing about 20 pounds. This is wrapped in brown paper and stacked in a specially insulated railway car for transportation to distant points, or into trucks for local delivery.

Of the liquid delivered to the press, 20 to 45 per cent is solidified; the rest turns to gas and must be reliquefied. The colder the temperature of the liquid CO_2 and the colder the press chest, the higher the percentage frozen. Based on heat content, it is found that it takes 3.75 pounds of liquid to produce 1 pound of solid. The expansion in the chest is due to atmospheric pressure.

The critical temperature[39] of carbon dioxide is 88° F. (31.1° C.), the critical pressure 1073 pounds. At 70° F. (21° C.), it is considerably below

[39] The critical temperature is the temperature just above which no pressure, no matter how great, can liquefy the gas; the critical pressure is the pressure which just suffices to liquefy the gas at the critical temperature.

the critical temperature, so that a pressure of 1000 to 1100 pounds suffices to keep it in the liquid state.

It will be clear that much of the expense in the plant will be that for recirculating the carbon dioxide gasified at the presses. The compressors are four-stage machines: 0 to 5 lbs., 65 to 70 lbs., 300 to 325 lbs., and 1000 to 1100 lbs. From the last stage the gas enters oil-removing filters, then a condenser cooled with tap water, which reduces its temperature to about 70° F. (21° C.). In the condenser, the carbon dioxide liquefies, and enters the "evaporator" with the new liquid, at the same temperature and pressure. Carbon dioxide from any source may be made into the solid form.

The uses of solid carbon dioxide are, at present, mainly for the preservation of foods. A railway car may be loaded with its perishable fruit, meat or vegetables, and a given number of blocks of "Dry Ice" placed on top of the goods so that the vapor will pass downward and form a heat-consuming blanket. The temperature attained is lower than with ice and salt mixtures, and may be regulated by the amount of "Dry Ice" per car. The shunting of the train to sidings for re-icing while en route becomes unnecessary; a single loading at the point of shipment suffices (for the average trip). Eighty-five per cent of the consumption is for ice-cream cooling. The effective refrigeration from 1 pound of solid carbon dioxide when subliming at 0° F. (−18° C.) is 244 Btu. A temperature as low as −108.8° F. (−87.9° C.) may be reached by allowing the solid carbon dioxide to evaporate at atmospheric pressure. A lower temperature still is obtained when evaporating at reduced pressure; hence a means is provided of reaching and maintaining low temperatures without any machinery.

In order to expand, the industry needs no machinery nor complicated processes of manufacture, but new uses, either as a refrigerant, or as a source of gas.

Quick Freezing of Foods

Refrigeration has been employed in the meat industry, in cold storage houses for the preservation of butter, eggs, vegetables, fruit, and other perishable foods. A new kind of refrigeration is now applied to sea foods, particularly fish fillets, and to fresh vegetables and small fruit; they are not only cooled, but frozen. The fillets of fish, for example, are laid in their packing paper, are held between two flexible non-corroding metallic belts, and pass between sprays of brine at −45° F. (−42° C.); they leave the belt frozen, to be stored or shipped at once. If to be shipped, the fillets may be packed in corrugated fiberboard boxes which insulate sufficiently to keep the fish frozen for 4 to 5 days, and fresh for several days longer. The frozen foods may be stored at temperatures low enough to keep them in the frozen state.

There is an increasing demand for house refrigeration, to keep its air temperature at a comfortable point. This subject is related to humidity relations, and is therefore discussed in Chapter 46.

Iceless Refrigerators. The various kinds of electric refrigerators which are displacing ice chests are operated on the same principle as the ammonia

refrigerating machine, but on a small scale. The working substance may be sulfur dioxide, methyl chloride, ammonia, a hydrocarbon, dichloro-difluoromethane, or other suitable agent; it is compressed by small motor-driven compressors. The heat of compression is removed by a current of air or by a trickle of water. The liquid so formed is then expanded, consuming heat which is drawn from the chest and its contents. The gas is then recompressed, and put through the next cycle.

Silica Gel Refrigerators. Other types absorb a vapor in silica gel,[40] or other solid absorbent, and use the heat of evaporation of the liquid for cooling. After the gel is saturated, its adsorbed mass is driven out by heat, thus revivifying the gel; in the meantime, a twin unit carries the load.

Other Patents

U. S. Patents 2,040,407 and 2,040,406, chemical heating composition, to produce heat by chemical action.

Problems

1. A swimming pool with an area of 25 feet by 70 feet contains water to an average depth of 7.13 feet. Find the cubical content and the weight of the water it contains. The water enters at a temperature of 45° F., and must be heated to 68° F. How many pounds of coal are needed to furnish that heat, if 73 per cent of the heat value in the coal reaches the water in the pool? How many gallons of fuel oil, if its specific gravity is 0.9, and the efficiency of heat transfer the same as for coal? For the same pool, at another season, the water enters at 32° F., and must be heated to 72° F. How many pounds of anthracite must be burned and used, if 73 per cent of the heat value in it reaches the water? All necessary heat values and conversion figures will be found either in this chapter or in the appendix.

2. Dry ice in Los Angeles can be made purer and just as cheaply from CO_2 from combustion of natural gas as from the gas wells developed in several places. This is due to the fact that the power which can be generated by burning natural gas under a boiler is just about sufficient to compress the CO_2 which can be recovered from the flue gas.

A dry ice plant burns natural gas (CH_4), absorbs the CO_2 formed in Na_2CO_3 solution, and recovers and compresses the pure CO_2, forming a 220-lb. cake of dry ice every 10 minutes.

(1) Assuming only 50 per cent of the CO_2 formed to be recovered, what volume (cu. ft.) of CH_4 is burned per hour? (60° F., atm. press).

(2) Assuming weights of 90 lb./cu. ft. for dry ice and 57 lb./cu. ft. for water ice, and refrigerating effects of 275 Btu. per pound, and 155 Btu. per pound, respectively, what weight of dry ice is equivalent to a ton of water ice, and what volume (cu. ft.) will each occupy?

(3) If dry ice costs $0.02/lb., what is the equivalent value of the water ice?

(4) If the soda liquor starts at 9.0 lb. Na_2CO_3/cu. ft. and 60 per cent is carbonated to $NaHCO_3$ and 20 per cent remains as $NaHCO_3$ at the discharge from the evaporator, how many cu. ft. of liquor (neglecting volume changes) must be carbonated per minute to handle the above production?

Reading References

"Diphenyl may solve reheating problem," G. B. Cunningham, *Power*, 72, 374 (1930), with a table of physical properties.

"Mercury vapor unit operates successfully at South Meadow," James Orr, *Power*, 72, 4 (1930).

"Fuel—solid, liquid, and gaseous," J. S. S. Brame, London, Edward Arnold, 1924.

[40] *Ice and Refrigeration*, 74, 217 (1928); 78, 331 (1930).

"A system of boiler water treatment based on chemical equilibrium," Ralph E. Hall, *Ind. Eng. Chem.*, **17**, 283 (1925).

"The use of mercury in power generation," A. J. Nerad, *Trans. Am. Inst. Chem. Eng.*, **28**, 12 (1932).

"The thermodynamic properties of dichloro-difluoromethane," Ralph M. Buffington and W. K. Gilkey, *Ind. Eng. Chem.*, **23**, 254 (1931).

"Pressure-total heat chart for dichlorodifluoromethane," Walter B. Lawrence, *Refrig. Eng.*, **24**, 286, Nov. (1932).

"Sulfur dioxide as a refrigerant," Chas. W. Johnson, *Ind. Eng. Chem.*, **24**, 626 (1932).

"Methyl chloride," J. B. Churchill, *Ind. Eng. Chem.*, **24**, 623 (1932).

"Mollier diagram for CO_2," prepared for *Refrigerating Engineering* from chart and investigations of Plank and Kuprianoff, whose paper appeared in *Z. ges. Kalte Ind.*; *Refrig. Eng.*, **20**, 33, July (1930).

"Liquid CO_2," Gustav T. Reich, *Chem. Met. Eng.*, **38**, 136 (1931).

"Solid carbon dioxide from by-product fermentation gas," C. L. Jones, *Ind. Eng. Chem.*, **23**, 798 (1931).

"Carbon dioxide and its solidification," Charles O. Duevel, Jr., *Refrig. Eng.*, July, 1931, p. 18.

"Machinery to make solid carbon dioxide," Terry Mitchell, *Ind. Eng. Chem.*, **23**, 523 (1931).

"Keeping duralumin rivets workable with Dry Ice," E. P. Dean, *Metals and Alloys*, **2**, 165 (1931).

"The manufacture of carbon dioxide," H. E. Howe, *Ind. Eng. Chem.*, **20**, 1091 (1928).

"Merits of carbon dioxide as a refrigerant," F. P. MacNeil, *Power*, **72**, 652 (1930).

"Cold treating Dural with CO_2," *Am. Machinist*, **75**, 439 (1931).

"Silica gel refrigeration system," *Ice and Refrigeration*, **74**, 217 (1928); **78**, 331 (1930).

"Refrigeration and the fishing industry," D. B. Finn, *Refrig. Eng.*, **20**, 287 (1930).

"History and present importance of quick freezing," C. Birdseye and G. A. Fitzgerald, *Ind. Eng. Chem.*, **24**, 676 (1932).

"Advances in the preservation of fish by freezing," H. F. Taylor, *Ind. Eng. Chem.*, **24**, 679 (1932).

"Symposium on refrigeration and refrigerants," *Ind. Eng. Chem.*, **24**, 601-686 (1932), with an introductory article by D. H. Killeffer.

"Certain chemical engineering aspects of the fishery industries," C. Birdseye, *Trans. Am. Inst. Chem. Eng.*, **24**, 245 (1931).

"The economic generation of steam in chemical works," F. H. Preece and B. Samuels, *Trans. Inst. Chem. Eng. (Br.)*, **12**, 144 (1934).

"The economic use of steam in chemical works," W. F. Carey and A. H. Waring, *Trans. Inst. Chem. Eng. (Br.)*, **12**, 158 (1934).

"The spontaneous oxidation of coal and other organic substances," J. S. Haldane and R. H. Makgill, *J. Soc. Chem. Ind.*, **53**, 359T (1934).

"A study of the absorption of sulfur dioxide from flue gases," Donald B. Keyes, *J. Soc. Chem. Ind.*, in *Chemistry and Industry*, **53**, 692 (1934).

"Conservation of coal resources," George S. Rice, A. C. Fieldner, and F. G. Tryon, *Third World Power Conference*, **1936**; section 4, paper 11.

"The trend of boiler design, as affected by factors internal to boilers," Perry Cassidy, Bull. 3-180, The Babcock and Wilcox Company, New York, 1935.

"Water-Cooled Furnaces," Bull. G-16, The Babcock and Wilcox Company, New York, 1939.

"The B&W direct-firing system," Bull. G-19, The Babcock and Wilcox Company, New York, 1936.

"More power for western industry," George C. Tenney, *Chem. Met. Eng.*, **45**, 472 (1938).

"Electrochemical power," with tables and a map, *Chem. Met. Eng.*, **45**, 462 (1938).

"Power requirements in electrochemical, electrometallurgical, and allied industries," Federal Power Commission, 1938.

"Water conditioning in steam generation," Everett P. Partridge and A. C. Purdy, *Ind. Eng. Chem.*, **31**, 387 (1939).

"Role of water in conquering fire in refining plants," Dawson Powell, *Petr. Ref.*, **25**, 513 (1946).

"Application of centrifugal refrigeration to ultra low temperatures," E. P. Palmatier, *Chem. Eng. Progress*, **44**, 481 (1948).

The inhabitants of a city must have a plentiful supply of water for drinking, cooking, washing, and sanitary purposes. It is one of the many public services to which the American can point with pride. The largest city in the country brings its water 92 miles—water which is palatable and safe at all periods of the year. The largest city on the West Coast brings part of its water over a distance exceeding 240 miles. A second problem which the congregation of so many people in cities has raised is that of sewage disposal; in its solution, it is gratifying to contemplate that an American chemist, Dr. H. W. Clark of the Massachusetts Board of Health, has played a major rôle by his discovery of the principles of the activated sludge process.

Chapter 13*

Water for Municipal and Industrial Use; Sewage and Industrial Waste Disposal

In every city, a supply of water is provided for domestic, public, and industrial uses. Chemical industries at times require water which meets certain specific requirements; in some cases it must be free from even traces of heavy metals; in others, its purity is of no moment, but it must be cold the year round. Industries situated within reach of city water draw their supply, or at least part of it, from the city main. For that reason, water for municipal purposes will be considered first, and subsequently the additional demands made by the industries.

Water for Municipal Purposes

Water for municipal purposes, for drinking, for general domestic and industrial consumption must be (1) hygienically safe, (2) reasonably soft, (3) practically colorless, and (4) free from objectionable odor and taste.

Absolutely pure water, consisting only of H_2O free from any dissolved matter, and optically void, is a laboratory curiosity, and most difficult to prepare; such a water would be soft, colorless, and odorless, and would have a pH value of 7.0. It is the last requirement which is difficult to meet, for traces of carbon dioxide lower the pH. Rain water collected in a cistern would be soft; it is still the custom in rural areas to build such cisterns in order to have water which soaps easily for the washing. In Bermuda, all potable water and water for washing is rain water, collected on the roofs of the dwellings. River and lake waters are surface waters; they are comparatively soft (that is, low in mineral content), and are most likely to contain easily soluble salts, and sediments. Ground waters, from deep wells, for example, are usually free from suspended matter, but are much harder (that is, richer in calcium and magnesium salts) than surface waters in the same vicinity. In regions of heavy rainfall, surface waters contain less mineral matter, because of dilution.

Sea water is not water at all, in comparison to the waters just discussed,

* In collaboration with Dr. George E. Symons, Associate Editor, *Water and Sewage Works*, New York City.

but a salt solution. It contains 3.5 per cent salts, of which 80 per cent is common salt, NaCl. This is an enormous concentration; nevertheless, sea water is used industrially, for example, in turbine steam surface condensers in plants located at the sea shore.

In surface waters and ground waters, the amount of impurities is so small that it is expressed not in per cent, but in parts per million (ppm.), as for example, 300 ppm., which means 300 grams of dissolved matter in 1 million grams of water (300 milligrams per liter). Roughly speaking, sea water is 100 times more concentrated.

In considering soft waters and hard waters, it is well to classify more closely, as in Table 41.

TABLE 41.—*Classification of Waters.*

Type	Concentration of total solids (ppm)
Soft	Less than 100
Medium hard	100 to 200
Hard	200 to 500
Saline	More than 500

"Parts per million total solids" means the residue on evaporating the water on a steam bath. The classification just given is quantitative; but to most chemists, hardness does not mean merely a comparatively larger amount of total solids, but the presence of salts of calcium and magnesium which, with a soap solution, prevent or inhibit foam formation until they are precipitated as insoluble soaps. In general it so happens that more than half of the residual solids for medium and hard waters are calcium and magnesium compounds, so that the figures reflect the amount of these salts as well as the total for all salts. With saline waters, it is different; here the total solids are likely to be mainly sodium chloride.

The production of water for municipal use involves three phases: procurement, treatment or purification, and distribution.

Procurement of Water. An adequate water supply is absolutely essential to the maintenance of modern civilization, and the importance of such a supply is evidenced by the distance to which modern cities go to obtain it.

When municipalities are located on large streams or fresh-water lakes, source of supply is no problem; but these being surface waters, they generally need purification before use. Some large cities find it necessary to go to great distances for their supplies; New York City and Los Angeles are outstanding examples, the former having five sources and the latter utilizing water from the Colorado River more than 200 miles away.

In smaller cities where ground waters are sufficient, water is obtained from wells, which may be from 20 to 1000 or more feet deep, depending on the strata from which the water is obtained. When deep wells flow under their own pressure, they are known as artesian wells. Because of the increased use of well waters in many areas, the ground water level has receded to a considerable extent in recent years and artesian (flowing) wells are infrequently found, but one in Texas has a reported flow of 25 million gallons

per day. Most wells have to be worked by pumps placed far down in the wells and operated by shafts connected to motors at ground level. The selection of pumps for deep wells is a science in itself.[1]

Well waters have the advantage of being cool, the temperature generally approximating the mean average temperature of the area. In the middle section of the United States, this temperature is from 52 to 54° F., an ideal temperature of water for drinking purposes.

Well waters have certain disadvantages. Since they will pick up soluble material through which they pass, most well waters contain appreciable amounts of calcium and magnesium salts and are therefore hard waters, which consume excessive amounts of soap and deposit unwanted scale in boilers. Some well waters also contain iron and manganese, both of which are undesirable; others contain appreciable amounts of carbon dioxide, which makes the water corrosive.

Purification of Water. Impurities and undesirable substances such as sediment, bacteria, and dissolved matter, may have a bearing on the choice of a water supply source, but their presence does not preclude use of the water, for all impurities can be removed by proper treatment.

Surface water requires removal of color, odors, suspended matter, and bacteria, and in some cases removal of hardness and the protection of the water against recontamination. Well waters usually require treatment only to safeguard the bacterial condition of the water, to remove carbon dioxide, and to soften when desired.

The standard treatment of surface waters includes coagulation, filtration, disinfection, and taste and odor removal, where necessary. Coagulation is accomplished by adding salts of aluminum or ferric iron to the water to produce a floc which by virtue of its chemical properties and physical nature precipitates colloids, and entraps foreign matter, color, turbidity, and bacteria to effect their removal by sedimentation. Proper mixing and flocculation is essential to good coagulation.

Sedimentation for several hours following coagulation allows the removal of these impurities. Where tastes and odors exist and where color is present, the addition of highly adsorbent activated carbon prior to sedimentation assists in the removal of these impurities. The addition of chlorine or chlorine dioxide is also helpful in eliminating tastes, odors, and color. Chlorine also aids in removing iron and manganese and improves coagulation as well as acting as a disinfectant. Properly operated coagulation and sedimentation processes will remove 85 per cent or more of suspended matter and bacteria.

Filtration through fine sand beds is frequently practised to eliminate the remaining turbidity and bacteria. When filters, which operate at relatively high rates (2 gal. per sq. ft. per min. and above), are not kept clean, bacteria may penetrate the sand and pass through the filter. It is for this reason that disinfection is practiced.

In most municipal plants disinfection is accomplished by the controlled

[1] "Selecting Deep Well Centrifugal Pumps," Axel O. Fabrin, *Water & Sewage Works*, p. R-87 (1946).

addition of chlorine. Chlorine dioxide is also a disinfectant, as are ozone and ultraviolet light. Ozone requires thorough mixing, and ultraviolet light is effective only when the water is clear, as these rays do not penetrate water to any great distance. Both of these latter methods of disinfection require cheap sources of electric power to be economical.

Distribution of Water. After such treatment as is necessary, the water may be stored in protected reservoirs and then distributed to consumers by pumping through large cast-iron pipes called mains. Pressure is maintained by pumps under continuous operation, or by pumping into elevated tanks. Most modern water works use electrically driven centrifugal pumps; older reciprocating steam pumping engines are gradually being replaced.

Disinfection. The addition of chlorine to water is generally for the purpose of disinfection, but its use frequently accomplishes improved coagulation and aids in removal of color complexes, iron, algae, manganese, etc. Chlorine in water reacts to form hypochlorous acid, which dissociates to a degree depending on the pH. Chlorine in water can react with inorganic and organic substances as well as with biological forms. When it is present as hypochlorous acid or hypochlorite ion, it is known as "free available chlorine," and may react by direct combination, oxidation, or coagulation of organic compounds. If free available chlorine reacts with ammonia, chloramines are formed and the residual chlorine as determined by ortho-toluidine test is called "combined available chlorine."

The chlorine demand of a water is the difference between the amount of chlorine added and the amount of residual chlorine remaining after the contact period. The bactericidal action of chlorine is generally considered to be of a physicochemical nature.

In treating water, chlorine may be added at one or more of several points in the water plant. When the chlorine is added to an unfiltered supply, the treatment is called plain chlorination; when the chlorine is added prior to any other treatment, it is known as pre-chlorination. On the other hand, post-chlorination is the addition of chlorine following any other treatment, and rechlorination is the addition of chlorine to the distribution system after previous chlorination.

In modern practice there are but two types of chlorination. Combined residual chlorination results when the chlorine reacts with natural or added ammonia to form combined available chlorine residual. Free residual chlorination is accomplished when sufficient chlorine is added to destroy the ammonia and produce a residual chlorine consisting of free available chlorine as hypochlorite ion.

Combined residual chlorination may be brought about by the addition of chlorine to water containing ammonium, the amount of chlorine added being sufficient to produce chloramines; or it may be accomplished by the chlorine-ammonia treatment, wherein definite amounts of ammonia are added in relation to the amount of chlorine used. Chloramines are produced and these have certain advantages of longer persistence in the distribution system and the avoidance of chlorinous tastes in water. This

treatment has been on the decrease since the discovery of break-point chlorination treatment.[2]

Free residual chlorination has been found to produce water with practically no bacterial content and free from chlorinous tastes and odors. Free residual chlorination may be accomplished by break-point treatment, wherein the amount of chlorine is sufficient to convert all of the ammonia or amines to nitrogen trichloride, which is lost to the atmosphere, after which the residual chlorine is present as the hypochlorite ion. During this treatment the residual chlorine will rise as chloramines are produced and will disappear when the nitrogen is converted to nitrogen trichloride. Thereafter the residual as free available chlorine will be proportional to the chlorine added.

Free residual chlorination may also be achieved by adding a large excess of chlorine and dechlorinating with sulfur dioxide, a bisulfite or other reducing agent. Regardless of the method used to obtain free available chlorine residual, the advantages to be gained are manifold; free residual chlorination is on the increase as a means of disinfection in water-purification plants.

Since 1943 another chemical has received some attention as a disinfectant. Chlorine dioxide, produced by the action of chlorine in a solution of sodium chlorite, was first used at Niagara Falls, N. Y. for the removal of tastes and odors.[3] It has been found effective for destroying phenol and chlorophenol tastes, and is a powerful bactericide as well. Because of the cost its use has been limited to taste and odor treatment, although interest grows in its use as a disinfectant. At Niagara Falls it was found that the alum dosage could be reduced and activated carbon dispensed with, thereby lowering the cost of operation.

Other disinfectants include bromine, which has mainly been used in swimming-pool operations. Ozone and ultraviolet light have been used, but because a cheap source of power is essential to economical operation, neither method has met with much favor. Philadelphia, Penna. is now in the process of installing a $2,000,000 ozone plant for the treatment of 36 million gallons daily. At Marseille, France, disinfection by ultraviolet light has been practiced for a number of years.

General Remarks on Water Purification. When a coagulant is needed to remove turbidity and suspended matter, aluminum sulfate is almost the universal choice; it is called "filter alum." The amount of filter alum required depends upon the turbidity, and to a considerable degree upon the temperature of the water, colder water requiring more.[4]

Salts of the alkali metals and alkaline earths are present in most waters; the most common are calcium, magnesium, sodium and potassium, combined with the bicarbonate, carbonate, sulfate, chloride, nitrate, and nitrite ions.

[2] "Chlorination—a 5-year Review," A. E. Griffin, *Jour. N.E.W.W.A.*, 58, No. 4, p. 322 (1944).

[3] Chlorine Dioxide Treatment of Water," Synan, MacMahon, Vincent; *Water Works & Sewerage*, 92, p. R-129 (June, 1945).

[4] *See* curves showing relation between amounts of coagulant, temperature of water, and turbidity of coagulated and raw water, "Water Purification," Joseph W. Ellms, New York, McGraw-Hill Book Co., 1928, 2d ed., p. 412.

The alkalinity is usually sufficient to precipitate aluminum hydroxide from added alum; but if it is not, an appropriate amount of milk of lime or soda ash is added.

The presence of 0.1 to 0.2 ppm. of iron is enough to be troublesome, especially in the staining of fabrics and plumbing fixtures. It also stimulates the growth of *Crenothrix*, a thread-like organism which decomposes iron and manganese compounds with the formation of their hydroxides, and gives the water a bad taste and odor. When iron is present, it is generally in the form of ferrous carbonate or bicarbonate. On exposure to the air these compounds oxidize, and insoluble ferric hydroxide is formed. As small a quan-

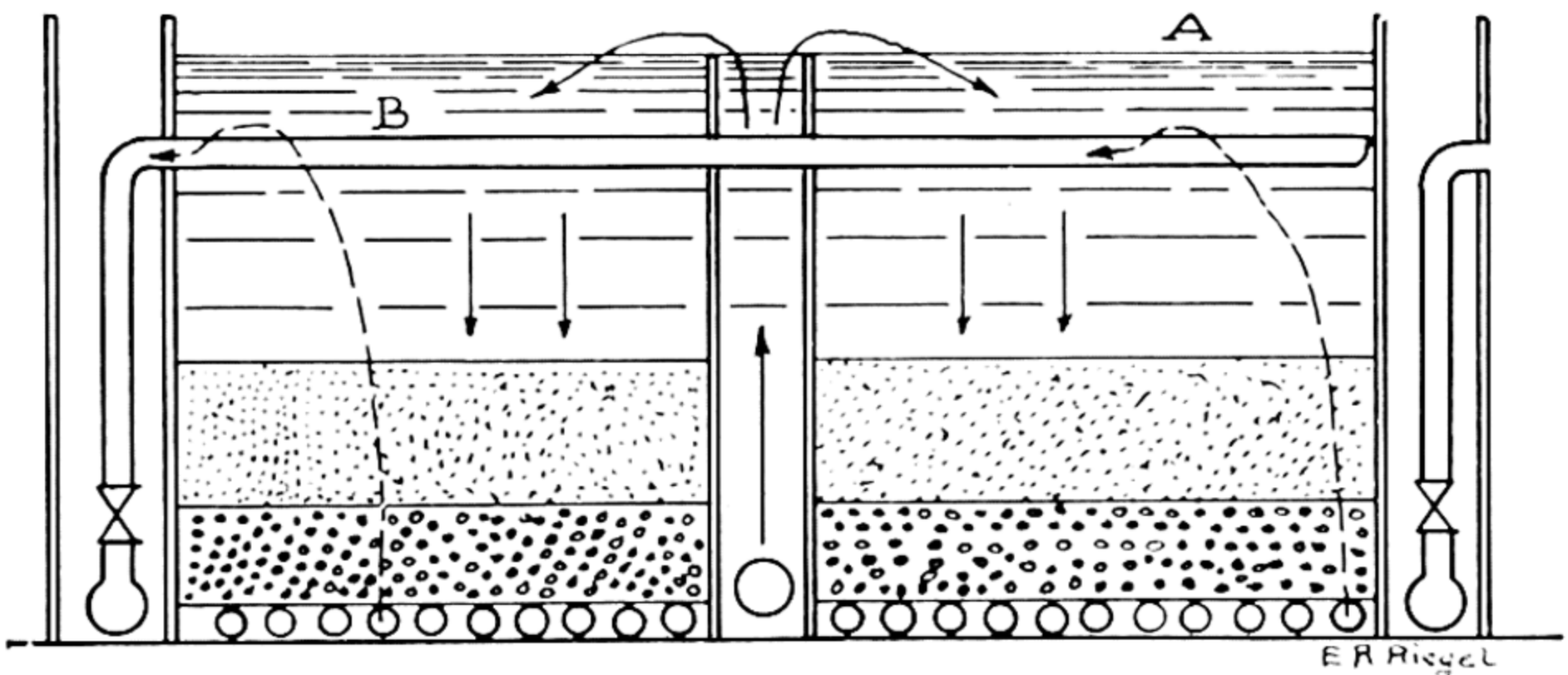


FIGURE 101.—Sand filter, to show method of washing. The water to be filtered enters as shown by full arrows, and passes through sand, gravel, and underdrains to clear wells (not shown); this water reaches level *A*. To wash, the flow is reversed; water enters through the underdrains, rises through gravel and sand, and leaves through gutter *B*. At such times, the level of the water stands at *B*. (Buffalo Filtration Plant.)

tity of iron as 2 ppm. forms a bulky and unsightly precipitate, sufficient to plug pipes. Iron may be removed by aeration (or by chlorination) followed by sedimentation. Aeration is accomplished by spraying the water into the air, or causing it to cascade over a bed of coarse material.

Tastes and odors are also removed by aeration; both are most frequently caused by algae, but may also come from industrial wastes, particularly phenol wastes. The removal of phenol from gas and coke plant wastes which might reach the municipal supply is described in Chapter 14.

Algae frequently give rise to the formation of a green scum in reservoirs and water mains; this must be removed mechanically, or better, prevented from forming by a chemical agent. Of the many algicides recommended, copper sulfate is the cheapest and most efficient.

The methods practiced for the purification of water for municipal purposes will be shown by means of several examples.

Buffalo Municipal Water Filtration Plant. For Buffalo, water is drawn from Lake Erie, at a point at the head of the Niagara River. The water enters a tunnel one mile long, 12 feet by 11½ feet in cross-section, through 12 ports, each 6 feet square, opening 20 feet below the surface of the lake. The tunnel runs into a canal which feeds the "low lift" centrifugal motor-

driven pumps which deliver the raw water to the coagulating basin against a head of 17 feet, through the raw water discharge conduit. In this conduit, twin Venturi tubes, 70 inches by 48 inches, meter the water. "Filter alum" is added at this point, at the rate of 50 pounds to 1 million gallons. The water is slightly alkaline, having an alkalinity equivalent to 100 ppm of $CaCO_3$, so that hydrous aluminum hydroxide, the alum floc, forms without other addition. The water moves slowly through the coagulating basin, taking a zigzag course set by baffle plates. The basin is 300 feet long, 100 feet wide, and 25 feet deep. After 3 hours, the water leaves it and passes to the sand filters.

There are 40 filters, each 53 feet by 33 feet in area. Perforated underdrain pipes are covered by 16 inches of gravel made up of five graded layers, and overlaid by 26 inches of sand (grain size 0.38 to 0.45 mm.). The filter capacity is 2 gallons per square foot per minute, 4 million gallons per day for the filter, and 160 million gallons per day for the plant. The filter capacity determines the capacity for the station; the low-lift pumps have a 50 per cent excess capacity, the tunnel a 180 per cent excess capacity. The filtered water passes to clear wells, and flows through a canal to the pumping station. Chlorine is injected in the canal, at the rate of 2 pounds per million gallons.

The reaction between the "filter alum" $Al_2(SO_4)_3 \cdot 14H_2O$ and the alkalinity in the water, in the form of calcium bicarbonate, is:

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(HCO_3)_3 + 3CaSO_4$$
$$Al(HCO_3)_3 \rightarrow Al(OH)_3 + 3CO_2$$
alum floc

The alum floc is voluminous; as it slowly settles, it carries with it most of the suspended matter, and a part of the bacteria (the count is reduced by about half). The choice of the coagulant is a particularly happy one in another respect. A part of it is in the colloidal state, with a positive charge in the colloidal sense, so that it is most efficient in precipitating the naturally occurring colloidal materials, particularly color, in the water, which are almost exclusively negative.[5]

In the clear water conduit a Venturi meter 12 feet by 6 feet records the volume of flow. The station is amply provided with level gages, meters, and pressure recorders; every filter has a set of instruments.

The suspended matter, including the alum floc, which does not settle out in the coagulating basin, is caught by the filter. After 15 hours, the filters are rid of their dirt by reversing the flow of the water, so that it rises through the sand and empties into gutters, which are submerged while the filter is working normally. This muddy water is delivered downstream from the intake. The washing requires 10 minutes. The coagulating basin is divided into two independent halves, so that it can be cleaned without interruption of the service; this is done twice a year. One and one-half per cent of the filtered water is consumed in washing the filter beds.

[5] The precipitation of a negatively charged colloidal suspension by a positively charged colloidal suspension is called mutual precipitation. The positive colloidal particle is $[Al(OH_3)]_nAl^{+++}$. For a closer study, *see* the chapter "Chemistry of Coagulation," in "Chemistry of water and sewage treatment," by A. M. Buswell, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1928.

The purified water is pumped through 60-inch mains and pressure is maintained by three 2-million gallon elevated tanks (steam standby pumps are available).

New York City. For New York City, more than 1.1 billion gallons per

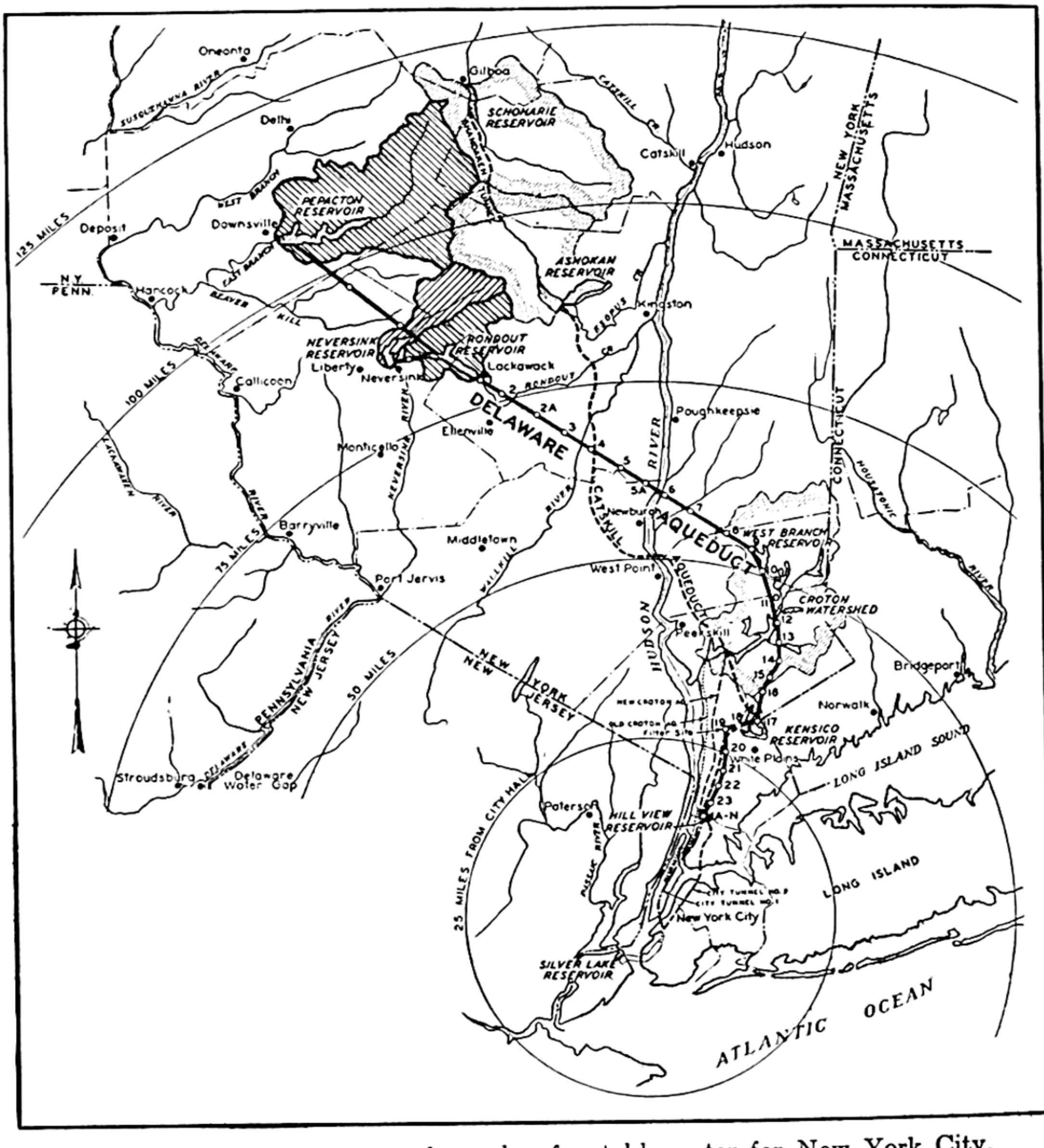


FIGURE 102.—The sources of supply of potable water for New York City. (The lightly shaded areas are the present watersheds; the cross hatched areas are under development in 1948). (The map is taken from *Water Works Engineering*, July 9, 1947, and reproduced by courtesy of Wm. W. Brush, Editor.)

day were supplied in 1947 from the following five sources: Catskill, surface water from Ahokan and Schoharie Reservoirs; Croton system, surface water from ten storage reservoirs; Delaware system, surface water by temporary use of Rondout Creek flow while reservoir is being constructed; Long Island

system, a mixture of surface and well water, but mainly well water. The Catskill system furnished 66 per cent of the total supply, the water being delivered through an aqueduct made up of hydraulic grade cut and cover sections, grade tunnel sections concrete-lined, and deep tunnel sections. Water flows under the Hudson river to the Kensico Reservoir and then to the Hill View Reservoir at the New York City line, for a total distance of 92 miles (see Figure 102). The Croton system supplies 30 per cent of the total.

Primary purification of the New York City water supplies depend upon processes effective during storage in the several reservoirs.[6] The efficiency of storage is high, and may be gauged from results observed with the Catskill supply. Thus the following removal efficiencies occur in Ashoken Reservoir: turbidity, 70%; color, 47%; organic nitrogen, 43%; inorganic nitrogen, 18%; hardness, 11%; iron, 56%; bacterial count (37 degrees, 24 hours), 84%; and Coliforms, 98%. The data above are based upon a recent three-year study.

Sufficient chlorine is injected at various points (65 in all) to produce a residual chlorine which is generally 0.2 ppm, with slight seasonal variations. The amount of chlorine injected differs somewhat at the several points, and also slightly with the season. The highest dosage is applied during the summer months. The estimated monthly dosage for the year 1948, for 20 stations, shows a low of 2 pounds per million gallons (pmg), and a high of 9 pounds pmg. For the Ashoken effluent, the dosage is varied between 2 and 3 pounds pmg; Croton lake receives 5 pounds pmg throughout the year. The Kensico effluent is treated with 3 pounds pmg for eight months of the year, and 4 pounds in the four months from June to September.

The Catskill water is aerated at both Ashokan (summers only) and Kensico by projecting it vertically into the air through about 1600 nozzles. The necessary head is furnished by gravity.

When algae growths require treatment, copper sulfate, an algicide, is applied to storage basins by dragging crystals in burlap bags suspended from a rowboat or motor launch, traveling back and forth over the surface. It has been applied by dry feed. At Muscoot Dam, Croton Lake, the algicide has been fed in continuously for several years by pumping a dilute solution through a 1000-foot pipe about one foot under the surface, with nozzles at a distance of every two feet. The average dosage is 1½ pounds per million gallons.

The Catskill water is distributed to the five boroughs by two circular tunnels cut in the rock below, and cement-lined. The original tunnel is 15 feet in diameter in the northern part of the system and 11 feet near its end. The tunnel lies 200 to 750 feet below the street. The second tunnel is 17 feet in diameter and is generally 500 feet below sea level for its entire length. Flow from one tunnel to the other may take place in Brooklyn

[6] All the information on the New York City water supply is based on data kindly supplied by Mr. John M. Cannella, Commissioner, Department of Water Supply, Gas and Electricity of the City of New York.

through user pipes. About every mile, pipe lines concreted in the construction shafts deliver the water to distribution mains.

Average characteristic analyses from various sources are given in the Table 42.

TABLE 42.—*Average characteristic analyses of the Catskill, Croton and Long Island water supplies for 1947.**

	Catskill	Croton	Long Island
Turbidity	2	2	2
Color	5	8	5
Odor	0	0	0
Nitrogen (ppm)			
Albuminoid ammonia	0.070	0.113	0.080
Free ammonia	0.040	0.078	0.158
Nitrite	0.001	0.001	0.000
Nitrate	0.10	0.13	1.86
Total solids (ppm) 100° F.	40	86	74
Fixed solids (ppm)	27	57	47
Chloride (ppm)	2.06	4.3	6.78
Hardness	17	50	31
Alkalinity (ppm)	8	35	9
Iron (ppm)	0.08	0.13	0.15
Hydrogen-ion, pH	6.9	7.4	6.7
Bacteria per ml	2	5	2
Coliforms/100 ml MPN	0.01	0.03	0.06
Total organisms—SU	63	220	124
Amorphous matter—SU	114	400	247
Typical Mineral Analysis:			
	ppm	ppm	
Silica (SiO_2)	2.4	6.3	
Calcium (Ca)	5.0	13.0	
Magnesium (Mg)	0.9	4.5	
Sodium (Na)	1.7	3.3	
Potassium (K)	0.7	1.3	
Carbonate (CO_3)	0	0	
Sulfate (SO_4)	9.7	17	
Fluoride (F)	0.03	0.05	

* Table supplied through the courtesy of the Dept. of Water Supply, Gas and Electricity, City of New York, John M. Cannella, Commissioner. All municipal water analyses record Coliform separately and in addition to the complete bacterial count, because it is an indicator of the presence of animal or human waste in the water.

Other Plants. New Orleans (Louisiana) takes its water from the Mississippi; the period for coagulation is 24 hours (compared to the usual period of 2 to 6 hours) because of the very fine sediment in the water. Kansas City (Missouri), using Missouri River water, which is highly turbid, uses presedimentation to remove the heavy suspended matter before flocculation and softening.

In Table 43, information on Colorado River water, as it is delivered to Los Angeles is presented.

WATER FOR INDUSTRIAL PURPOSES

In the further consideration of the supply of water for the industries, a number of requirements must be met. The most important is that the water should be cheap.

TABLE 43.—*Average analysis of softened and filtered Colorado River water furnished by the District to member areas during the year ending June 30, 1947: from a lime-zeolite softening and filtration plant, fed with Colorado River water. The District includes Los Angeles.**

	(ppm)
Silica (SiO_2)	12.6
Iron (Fe)	0.0
Calcium (Ca)	29.0
Magnesium (Mg)	14.0
Sodium (Na & K)	195.0
Carbonate (CO_3)	13.0
Bicarbonate (HCO_3)	57.0
Sulfate (SO_4)	333.0
Chloride (Cl)	98.0
Nitrate (NO_3)	0.3
Boron (B)	0.1
Fluorine (F)	0.5
Total dissolved solids	724
Hardness as $CaCO_3$	ppm
Total	130
Carbonate	69
Noncarbonate	61

* Kindly supplied by Mr. Julian Hinds, General Manager and Chief Engineer, The Metropolitan Water District of Southern California, Los Angeles 13.

Over half the water used in chemical plants is for cooling; it would be economically impossible to purchase city water, assuming that the capacity of the city system would be adequate. The composition for cooling water is of no great importance; its function is to carry away heat, by warming or by evaporation. Water fed to steel jackets forming the walls of a copper blast furnace, water flowing around a Cellarius vessel through which hydrogen chloride passes, and cooling water flowing through the jacket of a three-stage compressor illustrate the first; a trickle of water over an ammonia condenser, the second.

The water is drawn from a near-by river or lake, and passed through a pressure-type sand filter to remove any suspended matter which might clog pipes and valves. A fish trap protects the pump, which may be a Connersville blower or a centrifugal pump. The sand filter is similar in construction and operation to the gravity type described, except that it is contained in a cylindrical steel shell, either horizontal or vertical. The water enters at the top and leaves at the bottom, through a riser which brings the water to an elevated tank, from which it is fed to the parts to be cooled by gravity. The capacity of the pressure sand filters vary with the size, from 500 to 36,000 gallons per hour.

If available river water is not cool enough, wells may be driven; these frequently have maintained a flow of water of 54° F. (12.2° C.) the year round. The temperature of ground water generally is the same as the mean annual temperature.

Filtering may be dispensed with, if the piping is short and accessible; brackishness does not matter if the vessels to be cooled are stoneware. In the case of cast iron and steel, an occasional replacement because of cor-

rosion by the cooling water may be preferable to an elaborate installation for treating it.

Another considerable volume of water is used in the chemical plants for solution and dilution; as a rule, a reasonably pure river water is all that is needed.

These water requirements are usually readily met, because chemical plants are purposely located near an abundant supply of water, to be had for the pumping costs.

Water Softening. In dye application plants, in commercial and hospital laundries, in rayon plants, and others, the water used in processing must meet more rigid requirements. As a rule, it must be soft. If the only available supply of water is hard, the water must be treated to remove dissolved calcium and magnesium salts. This is done by means of (1) lime and soda ash addition, followed by settling and filtering, or (2) trisodium phosphate addition, or (3) contact with zeolites. The softening of water for use in steam boilers has been discussed in the preceding chapter; some supplementary remarks will be given here.

(1) The reason for combining the lime with the soda ash treatment is as follows: The carbonate hardness (formerly called temporary hardness) leads to the reactions:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O,$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O.$$

The magnesium carbonate is fairly soluble (100 ppm.) and requires an excess of lime:

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3.$$

The magnesium hydroxide is insoluble, as is the calcium carbonate, and both settle out. If magnesium chloride is present, the reaction

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

takes place, and although magnesium hydroxide precipitates, an equivalent amount of calcium chloride is in solution; no true softening has been achieved. Accordingly, sufficient soda ash is added to precipitate the calcium chloride, as well as any calcium chloride, nitrate, or sulfate originally present, which remain unattacked by lime:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl, \text{ or}$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4.$$

All the dissolved salts mentioned in this paragraph except the bicarbonates make up the non-carbonate hardness; only the calcium sulfate is scale-forming, but any of the others will bind soap or dyes. It should be understood that the magnesium sulfate undergoes the same reactions as the chloride.[7]

It is clear that the amount of lime and soda ash will be determined by the analysis of the water, supplemented by the actual results of the treatment. A large installation for softening would resemble a municipal filtra-

[7] For a more detailed treatment, *see* the chapter on "Lime and soda process" in "The chemistry of water and sewage treatment," A. M. Buswell, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1928.

tion plant. On a smaller scale, two tanks may be used; in one, the raw water receives the dosage of chemicals, and after stirring, is left to settle; in the meantime, the other may be drawn off, only the comparatively clear water passing to the sand filter, while the main part of the precipitate is run to the sewer. Hot water is frequently employed; the treatment and settling take place in a large tank; here again, only the clear supernatant water passes to the filter. In the case of hot water, the action and the settling

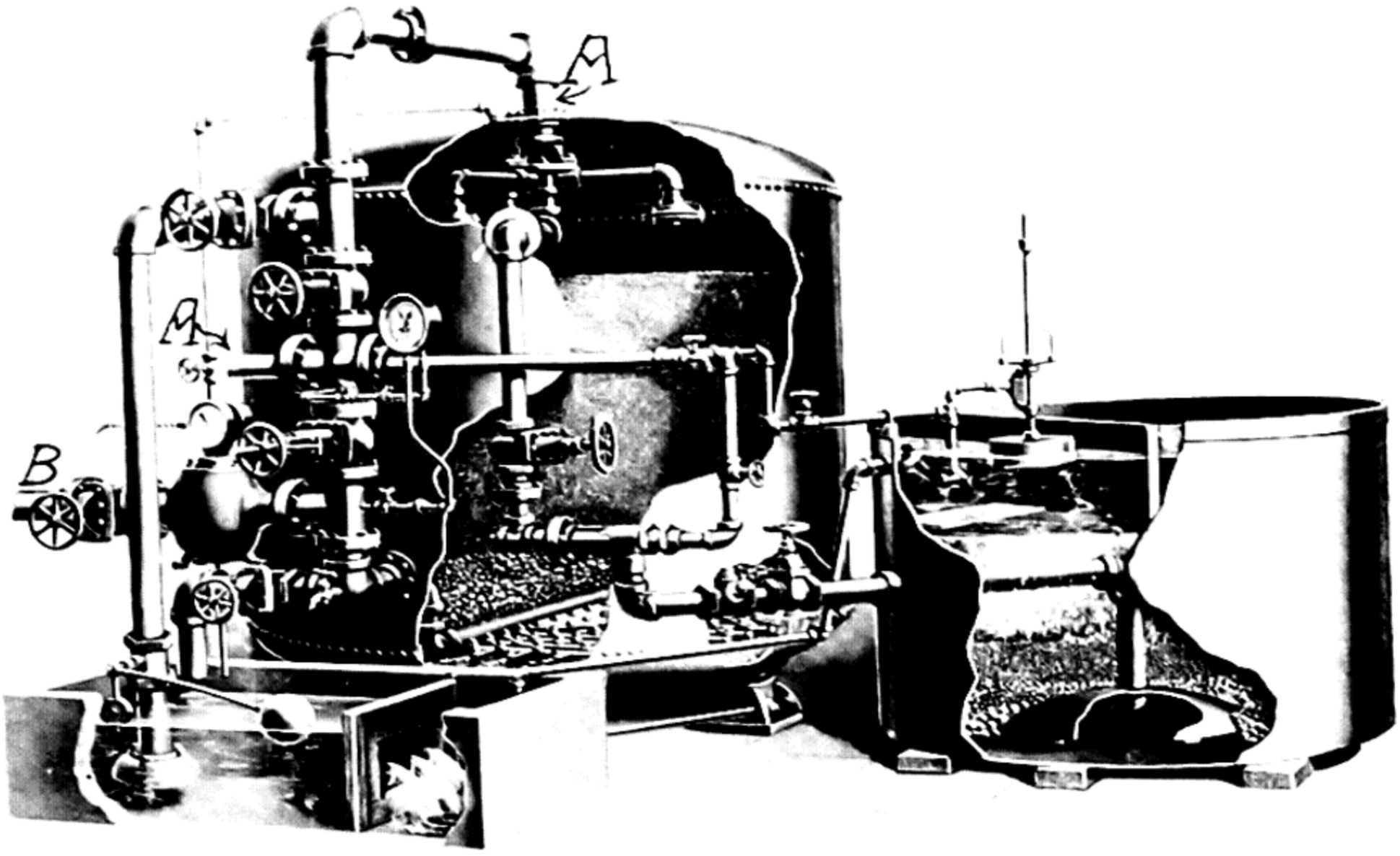


FIGURE 103.—Permutit vertical zeolite water softener, pressure, downflow type, showing the zeolite bed in the softener. Raw water inlet *A*, treated water outlet *B*, brine tank with bed of salt, and brine pipe with ejector from bottom of brine tank to the distributors at top of zeolite tank. (Courtesy of The Permutit Co., New York.)

of the precipitate are more rapid. In an hour, an effluent with only 25 ppm. is obtained. The application of trisodium phosphate, (2), an alkaline substance, is similar.

(3) In contact with zeolite,[8] the following reaction takes place:

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3$$

The symbol Ze stands for the zeolite radical: $2SiO_2 \cdot Al_2O_3 \cdot Na_2O$, which is now written Na_2Ze. This is preferable, because a zeolite containing 2 molecules of SiO_2 is not suitable, and must be replaced in practice with zeolites containing from 5 to 13 molecules of SiO_2. The water gives up its calcium and receives an equivalent amount of sodium. After 6 to 8 hours, the flow of raw water is stopped, and the container filled with brine (saturated sodium chloride solution). (*See* Figure 103.) The reaction

$$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$$

takes place, in a period which was originally 6 hours. After that time, the

[8] For the manufacture of these, *see* U. S. Patents 1,343,927 and 1,304,206.

salt solution is drawn off, the vessel rinsed, and the raw water sent in. The "hardness" in the form of calcium and magnesium chlorides passes out with the salt solution. Improvements in the manufacture of zeolite have led to the rapid type of exchange material, the gel type or porous type; the softening action is more rapid, and the regeneration also (30 minutes). The apparatus for softening resembles the pressure sand filters, with zeolite in grain form instead of the sand. It has been found that upflow as well as downflow may be practiced; with upflow a greater softening capacity is reached.[9]

A successful commercial zeolite is made from New Jersey greensand (glauconite), by special treatment. The softening capacity for greensand type zeolites is from 2,800 to 5,000 grains (as $CaCO_3$) per cubic foot of zeolite (weight 85 to 92 lbs. per cubic foot); for the synthetic types, up to 10,000 grains per cubic foot of zeolite (weight 50 to 60 lbs. per cubic foot). The effluent may be as low as 5 ppm. or less in hardness.

A plant which draws its own water from a river would send a portion of it through the zeolite softeners or lime-soda ash system, for use in its boilers, or in the washing, dissolving or diluting operations which call for soft water. The greater part of the water supply would serve untreated.

Among the new zeolite developments there should be mentioned "Zeo-Karb," a high-capacity carbonaceous zeolite. It is made from coal, lignite or wood, by treatment with oleum, chlorsulfonic acid or other agents, then washed, "stabilized," and screened to size. "Zeo-Karb" can function in the sodium cycle, taking up calcium and magnesium from the water and giving it sodium in exchange; the revivification is by treatment with salt solution. But it may also function in the hydrogen cycle, in which the metal ions, calcium, magnesium and sodium, leave the water to be replaced by hydrogen ions; the revivification is then by dilute acid treatment. In waters containing calcium bicarbonate, which are very common, the hydrogen zeolite removes the calcium ion, and produces H_2CO_3, which may be driven out in a degasifier (by air blow, or by vacuum), resulting in complete removal of the original bicarbonate.[10]

The Deionization of Water. In the last twenty years great progress has been made in the variety, service and number of ion-exchange adsorbents, generally under the spur of necessity. Inorganic exchangers of the siliceous type cannot be used in low pH waters because their lattice disintegrates in such waters or solutions. It was discovered that a number of synthetic resins (and certain natural materials as well) of special composition have ion exchange power.[11] A group of such resins function either in the sodium cycle or the hydrogen cycle; for the sodium cycle, the resin is regenerated with a sodium chloride solution, while for the hydrogen cycle, the spent resin is regenerated with dilute sulfuric acid or hydrochloric acid. Polyhydric phenols condensed with formaldehyde owe their cation exchange

[9] "Recent developments in zeolite softening," A. S. Behrman, *Ind. Eng. Chem.*, **19**, 445 (1927). "Zeolites, mining, processing, manufacture, and uses," Eskel Nordell 9th annual Michigan Conference on water purification, Bull. 61, Jan., 1935.

[10] "Carbonaceous zeolites, an advance in boiler-feedwater conditioning," by Howard L. Tiger, *Trans. A.S.T.M.*, pp. 315-325, 1938.

[11] "Absorptive properties of synthetic resins: Part I.", B. A. Adams and E. L. Holmes, *J. Soc. Chem. Ind. Trans.*, **54**, 1 (1935).

power to the phenolic hydroxyl groups. By condensing *o*- or *p*-phenolsulfonic acid with formaldehyde, resins are formed which have cationic exchange ability, thanks to their sulfonic acid groups; such resins function both in the sodium and in the acid cycle.[12]

In the hydrogen cycle, calcium, magnesium or sodium is replaced by a hydrogen ion, leaving an acid in the water or solution. Efforts to develop an exchanger mass which would remove the anion have been richly rewarded; the anion is removed by any one of several novel masses, although it may well be that it is the acid molecule as a whole which is removed. The anion exchange masses include synthetic resins made by condensing *m*-phenylene diamine with formaldehyde, the resin formed being fortified by incorporating alkyl groups into the polymer. Other amine-formaldehyde, and tanning-formaldehyde resins have anion exchange power.[13] Let the original cation exchange in the hydrogen cycle be depicted as follows:

$$\text{(Hydrogen) (resin polymer)} + \text{Metal}\cdot\text{Cl} \rightarrow \text{Metal}\cdot\text{(resin polymer)} + \text{HCl}.$$

In the anion exchange mass, the newly formed acid is adsorbed:

$$\text{(resin polymer)}\cdot\text{NH}_3 + \text{HCl} \rightarrow \text{(resin polymer)}\cdot\text{NH}_3\text{Cl}$$

The anion exchanger is regenerated by means of a solution of soda ash or caustic soda.

The removal of both the cation and the anion of the dissolved electrolyte impurity is called "demineralizing" or "deionizing." There are large-scale three-story applications of demineralization, in which 1,000 gallons of water per minute are produced. The raw water is filtered, and then pumped to wooden tanks on the third floor which contain the cation exchange mass (such as "Zeo-Karb H"). The effluent flows by gravity to the wooden tanks on the second floor which contain the anion exchange mass (such as "De-Acidite"), in which the anion is removed. The final water is collected on the first floor and pumped to service. It is found that deionized water is as pure as distilled water:

TABLE 44.—*Comparison of raw water and the same water after deionizing, and for another batch, after distillation.**

	Raw Water	Deionized	Distilled
Total dissolved solids (ppm)	117.9	6.9	3.9
Volatile matter (ppm)	39.6	2.5	2.6
Inorganic matter (ppm)	78.2	4.4	1.3
Iron (ppm)	0.07	0.01	0.25
Silica (ppm)	2.0	2.0	0.25
pH	6.9	6.7	6.3
Conductivity (reciprocal ohms)		3×10^{-6}	7×10^{-6}

* "Ion exchange resins, new tools for process industries," Frederick J. Myers, *Ind. Eng. Chem.*, 35, 858 (1943).

Such very pure water is required for example in the Thermofor catalytic process bead plant (Chapter 24). It will be noted that the silica is high;

[12] "Improved synthetic ion exchange resin," W. C. Bauman, *Ind. Eng. Chem.*, 38, 46 (1946).

[13] "Synthetic resins as exchange adsorbents," Robert J. Myers, John W. Eastes and Frederick J. Myers, *Ind. Eng. Chem.*, 33, 697 (1941).

if it must be lowered, it is given a special supplementary treatment by caustic-regenerated, specially prepared, highly basic anion exchange resins.[14]

The ion-exchange synthetic resins are solids resembling sand; the granules are 1 millimeter or so in diameter. They may be light brown ("Amberlite IR-4B"), dark purple, dark red, etc. The newer synthetic resin ion-exchange adsorbers have increased mechanical and chemical stability. They differ from one another in the length of service they offer. A resin must not be expected to do everything which may be required; it is rather necessary to adopt a resin, by its preparation and choice of components, to the intended duty.

All ion exchanges described in this section or in the preceding one take place at ordinary temperature.

Ion-exchange Adsorbers in Services other than Water. New and startling applications of ion-exchange materials have been made, of which only a few will be mentioned. The purification of sugar juices in order to lower processing costs and to produce an edible molasses is described in Chapter 23. Formaldehyde made by the partial oxidation of methanol may be purified of its objectionable formic acid content by ion-exchange treatment.[15] Tartrates are recovered by means of ion-exchange resins; the free acid is adsorbed, and later recovered as the sodium salt when the exchange material is regenerated.[16]

A simple classification such as the following may be acceptable as a summary.

(1) Cation exchangers.
   (a) Zeolites, natural or synthetic siliceous compounds, which take up calcium, for example, and replace it by sodium.
   (b) Carbonaceous masses, such as "Zeo-Karb," which take up calcium and release hydrogen.
   (c) Resinous material, made for example by condensing polyhydric phenol with formaldehyde, or condensing *p*-sulfonic phenol with formaldehyde. Calcium is accepted, and replaced by sodium, when the resin must be regenerated by sodium chloride; or hydrogen is released, when the resin must be regenerated by dilute acid.
(2) Anion exchangers, more correctly, acid adsorbents.
   (a) Inorganic masses, such as dolomite, or heavy-metal silicates.
   (b) Organic synthetic resins, such as a polyamine formaldehyde condensate, whose activity is derived from its amino groups. Example, "Amberlite IR-4B."[17]

It may be well to enumerate the requirements of waters to be used in certain important industries. Boiler water should be as soft as possible, to prevent incrustations on boiler plates and tubes. Water to be used in

[14] "Five ways to remove dissolved silica from boiler feedwater," M. E. Gilwood, *Power* (August, 1947).

[15] "Purification of formalin by ion-exchange treatment," George A. Cristy and Richard E. Lembcke, *Chem. Eng. Progress*, 44, 417 (1948).

[16] "Tartrates from grape wastes," J. R. Matchett, R. R. Legault, C. C. Nimmo, and G. K., Notter, *Ind. Eng. Chem.*, 36, 851 (1944). Read also: "Ion-exchange refining of dextrose solutions," M. Handelmann and R. H. Rogge, *Chem. Eng. Progress*, 44, 583 (1948). "Purification of formalin by ion-exchange treatment," George A. Cristy and Richard E. Lembcke, *Chem. Eng. Progress*, 44, 417 (1948). "Ion exchange develops as a unit process," *Chem. Industries*, 62, 754 (1948).

[17] U. S. Patent 2,402,384.

laundries should be relatively soft and free from iron and manganese. Paper mills require that a water be free from iron, since this stains the paper, and an excess of calcium and magnesium is to be avoided because they tend to precipitate the rosin soaps which are used in sizing the paper. Water containing sulfates, alkali carbonates, nitrates, and bacteria must be avoided in sugar refineries if the sugar is to crystallize well, is not to be deliquescent, and is not to decompose while standing in storage.

Alcohol distilleries require a cool water containing few microorganisms and relatively little sodium and magnesium chlorides. Bakeries require a potable water with a minimum of organic matter which might affect the action of yeast. Water to be used in dyeing should be free of iron, and contain little hardness in order to avoid the formation of insoluble lakes, which give impure shades and often spot the fabric. Wool and cotton mills require a very soft water in order that undue amounts of soap will not be wasted in washing the yarn. Viscose silk plants must have water absolutely free from copper. The soft beverage trade usually uses water which has been sand-filtered, chlorinated, and then filtered through activated carbon to remove tastes and odors; also, if the alkalinity is high, lime softening is practiced to reduce it.

"Heavy water," that is, water containing the heavy hydrogen isotope deuterium (mass 2) instead of hydrogen (mass 1), plays an important rôle in atomic fission work, but as yet has no other industrial uses.

Sewage Disposal Plants

Sewage may be defined as any waste discharged with water from households, habitations of any kind, manufacturing plants, and city streets. Its composition varies according to origin and methods; its ultimate disposal depends on its composition and on the size and type of the body of water which receives the waste.

Because of the growing interest in conservation and health, the treatment of sewage and of industrial wastes has become extremely important. The present discussion of the subject will be limited to a general description of processes, with typical examples.

Sewage may be disposed of by two methods; without treatment, and with treatment. When *disposal* of sewage is *without treatment*, it is known as disposal by dilution. This is a simple method, utilizing only some screens to catch large, coarse objects; the apparatus is of little importance. If the flow of the water course is 7000 gallons per capita per day, disposal by dilution has been permitted; but this method is becoming less and less acceptable. Even the large cities on the oceans are now using chlorination as well as screening to prevent pollution of bathing beaches.

When sewage is disposed of *with treatment*, there are three processes involved and one by-product process. These processes are: Primary Treatment; Secondary Treatment; Disinfection; and Solids Disposal.

Primary Treatment. Primary treatment consists of the removal of suspended matter by physical and mechanical means. It may include screens (of large and small openings and with or without mechanical clean-

ing) as well as sedimentation basins where the velocity of flow is controlled, to allow the settlement of sand and grit, followed by tanks in which the lighter organic solids are precipitated. (The velocity of flow is much slower for this tank than for the grit removal.) Primary treatment will remove as much as 55 per cent of the suspended matter in sewage, and as high as 35 per cent of the oxidizable organic matter.

Aids to the primary treatment process may consist of mechanical flocculation or chemical coagulation, both of which increase the amount of suspended solids removed in primary treatment.

Secondary Treatment. After primary treatment, the organic matter remaining in sewage is largely colloidal in size, although some of it is in true solution. Secondary treatment is a process of precipitating the colloids on biological surfaces and oxidation of the organic matter by the biological slime.

There are two means of carrying out secondary treatment. One is the trickling filter, consisting of rocks over which the settled sewage is sprayed at intervals. During the course of the flow of the settled sewage over the surface of the biological slime attached to the rocks, the organic matter precipitates and is oxidized.

The other method of carrying out the secondary treatment is known as the activated sludge process. In this process, the biological slimes form as flocs and are maintained in suspension in a tank by blowing air through the suspension. This air also furnishes the oxygen necessary for oxidation by the biological slime of the organic matter precipitated on the surface of the flocs.

Aids to the trickling filter in the secondary treatment process include high rate distribution with recirculation, in one or two stages; and in the activated sludge process, distribution of sewage input or tapered aeration are aids to increasing the efficiency of operation.

Secondary treatment process will remove practically all the suspended matter and all but a few per cent of the oxidizable organic matter in the sewage.

Disinfection. Addition of chlorine to sewage is primarily for the purpose of killing bacteria, but chloride also aids in odor control, in preventing poor operation of the activated sludge process, and otherwise helps operation. Disinfection or the killing of practically all the pathogenic bacteria in sewage requires addition of enough chlorine to satisfy the chlorine demand and to leave a small residual for a period of fifteen minutes or so. Contact may be provided by adding the chlorine prior to sedimentation in the case where only primary treatment is used, or may be added to a contact tank following secondary treatment. When chlorine is added in the sewers some distance from the treatment plant, it is known as upsewer chlorination, and is generally for the purpose of preventing the formation of hydrogen sulfide.

Solids Disposal. Solids are separated from sewage on the screens, in the grit chambers and in the primary sedimentation tanks. Solids are also produced in the secondary treatment process and must be removed before

the liquid is discharged to the final body of water. These solids must all be disposed of because they will otherwise putrify and cause a nuisance.

Screenings may be buried, or ground and returned to the liquid to settle out in the primary sedimentation tanks, or they may be burned. Grit, which if properly cleaned contains but a small amount of organic matter, may be used for fill, or if unusual amounts of organic matter (garbage particles) are present, the grit may be buried or passed through incinerators.

Organic matter which settles out in the primary tanks (raw sludge) is usually transported to digestion tanks where under the influence of bacteria in the absence of oxygen, the organic matter is converted to carbon dioxide and methane. This process of digestion reduces the amount and volume of the sludge solids, and stabilizes the remaining organic matter, so that nuisance conditions will not exist when the sludge is removed for drying.

The digested sludge may be dried on sand beds, or it may be dried and burned in incinerators. In some instances the dried sludge is used for soil conditioning. Undigested sludge from the activated sludge process has approximately 6 per cent nitrogen content. It has the highest value for conditioning and fertilizing.

The gas produced by digestion is high in heat value (approximately 640 Btu. per cu. ft.) and is generally used for heating around the sewage works. These gases are used to run gas engines in some cases for the purpose of operating blowers to aerate the sewage in the activated sludge process. The gas is sometimes used to heat boilers, which in turn furnish heat to keep the digestion tanks at optimum temperatures, thereby insuring better digestion of the sludge particles (85 to 92° F. is considered optimum).

In certain plants, the digestion is also carried on in the bottom compartment of a tank, the upper story of which acts as a sedimentation tank. This is the Imhoff tank. There have been modern adaptations of this tank. The Imhoff tank was an improvement over the septic tank, which today is used only for small installations where sewer systems are not provided. The septic tank has low efficiency because it combines sedimentation and digestion in the same tank.

In the more recent designs of sewage-treatment plants, separate sedimentation and sludge digestion has been provided. The Imhoff tank is no longer as popular in the United States, but remains as a good example of the forward steps in sewage treatment in this century.

The sewage disposal plant for the city of Worcester, Massachusetts (200,000 inhabitants), is an installation of Imhoff tanks on a grand scale. The plant can be seen from U. S. Highway No. 20. The functioning of the tanks is essentially like that of the smaller plant described. The raw sewage passes through the following divisions: grit chambers (2); screens (2); Imhoff tanks (12), each one of which is 32 feet deep, 50 by 50 feet in area, and divided into 4 parts; the direction of flow is reversed once a month; dosing tanks (8), for the distribution of the partially clarified sewage upon the trickling filters; trickling filters (4), on a lower level, and covering 13.68 acres; final settling tanks (4), to remove suspended matters from the effluent coming from the trickling filters. No chlorination is neces-

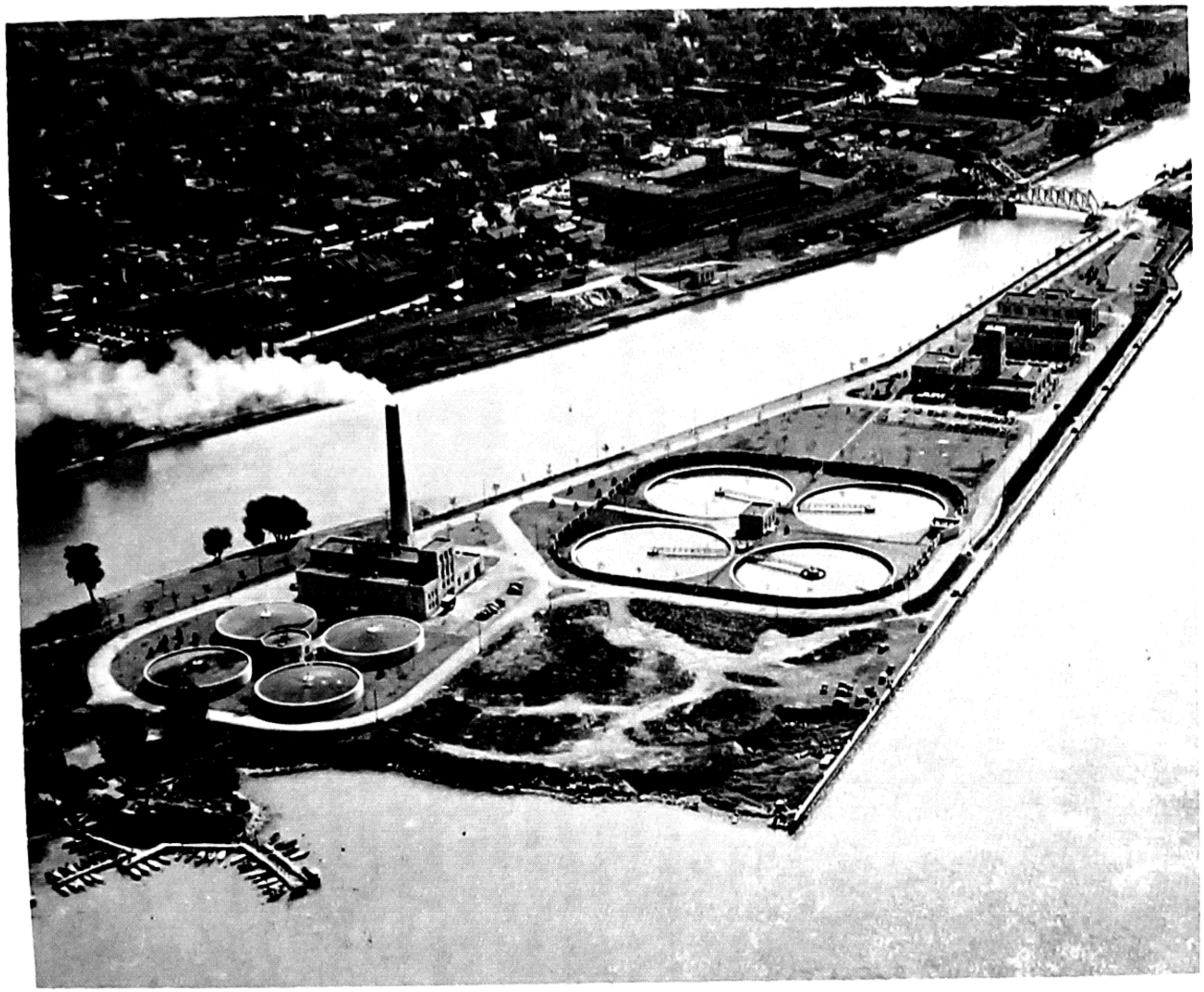


FIGURE 104.—Air view of the Buffalo sewage disposal plant, with four sedimentation tanks, four sludge digestion tanks and incinerator close by. The outfall from the four thickeners, visible at right of center and between them, is chlorinated. The outfall is to the Niagara river. The quiet water at the left is the Erie Barge Canal. (By permission.)

sary; the effluent discharged into the Blackstone River may be kept indefinitely in a closed bottle at room temperature without developing any disagreeable or offensive odor. The quantity of sewage normally handled is between 17 and 24 mgd. The Imhoff tanks remove 56 to 62 per cent of the total solids. The appearance of the plant is that of a city park.

Figure 104 shows a modern plant (the municipal plant at Buffalo, N. Y.) where primary treatment and disinfection are practiced and in which the

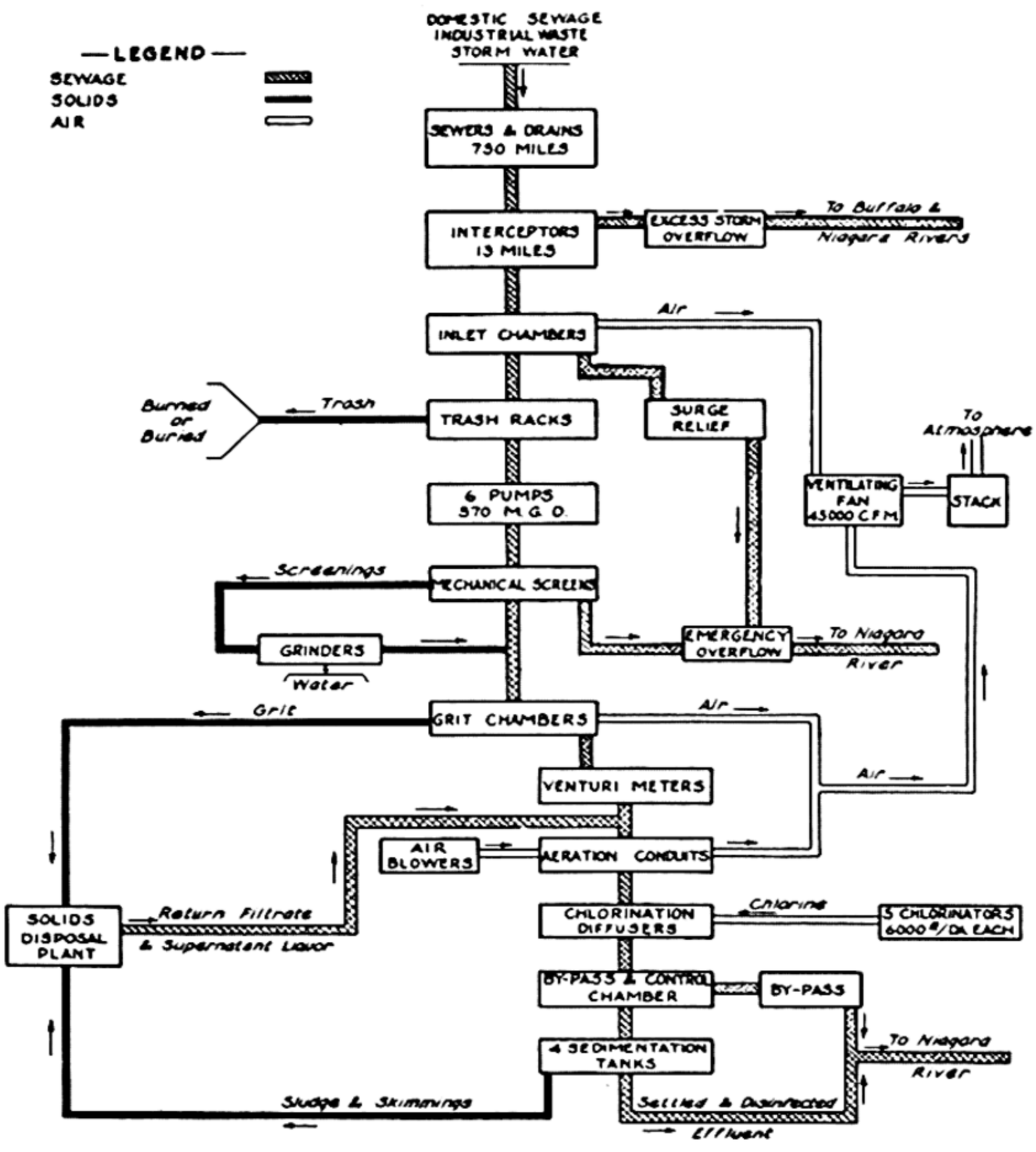


FIGURE 105.—Flow sheet for sewage treatment in Buffalo Sewage Treatment Works. (By permission.)

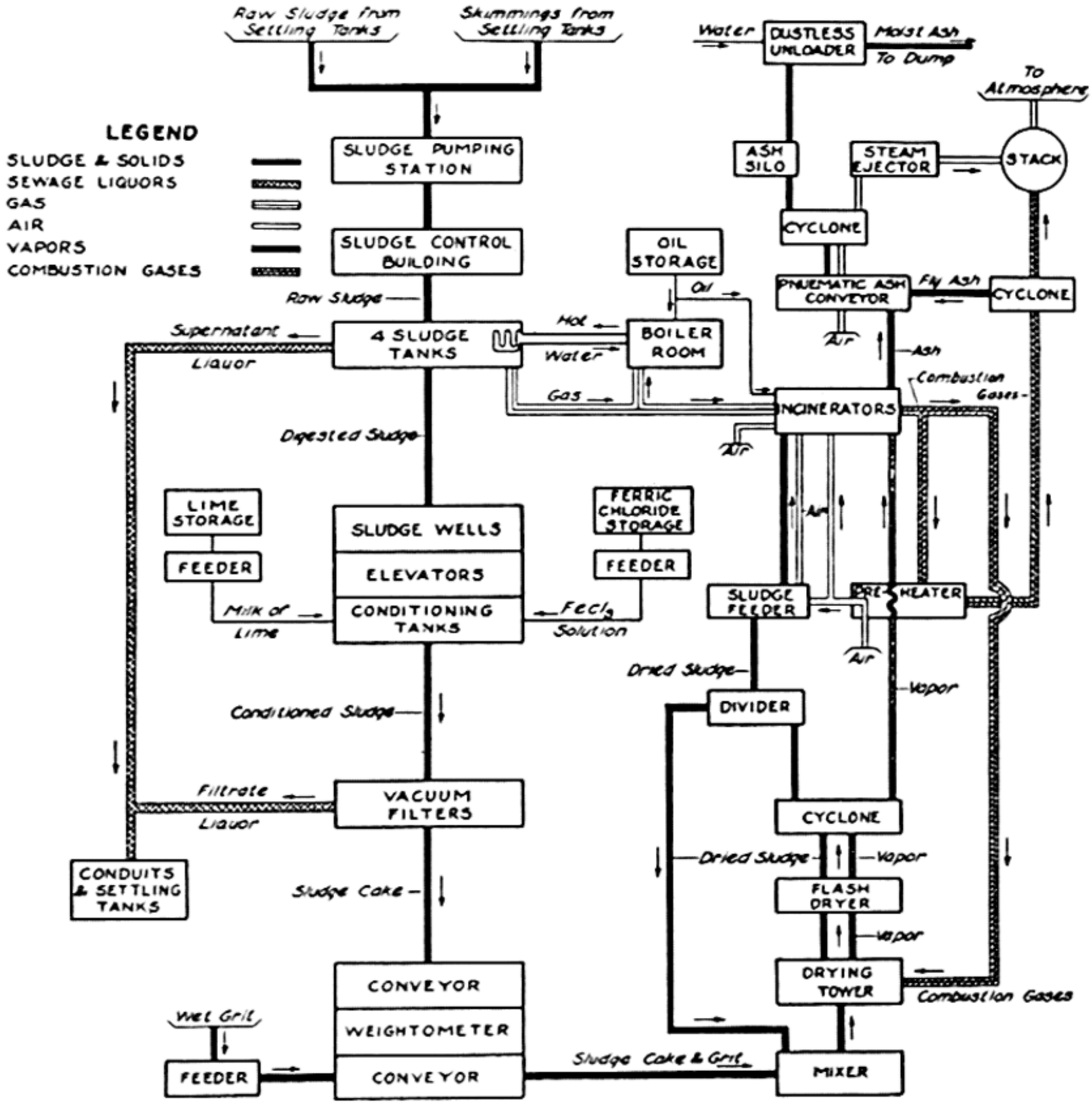
sludge is digested in separate tanks. The gas produced is equivalent to approximately 1 cubic foot per capita per day. The flow sheet for this treatment works is shown in Figure 105, and the flow sheet for the sludge disposal process at Buffalo in Figure 106.

ACTIVATED SLUDGE PROCESS

The activated sludge process "consists of the aeration of sewage in the presence of nitrifying and other organisms attached to the circulating sludge. It rests upon observations made in the course of a study of the

effect upon fish life of water polluted to different degrees by sewage and other substances."[18] The process can be best explained in terms of an actual plant.

The Milwaukee Plant. The activated sludge process differs from the Imhoff tank and similar procedures in that it employs microbial growth under aerobic condition. Air is supplied, and the material is exposed to the open air in large, rather shallow tanks through which it travels slowly.



FIGUSE 106.—Flow sheet for solids disposal plant, Buffalo Sewage Treatment Works. (By permission.)

Whatever action takes place in the digestion tanks of the Imhoff system is anaerobic (that is, without oxygen). Another difference is that the removal of organic matter is practically complete in the activated sludge process, whereas the removal of organic matter in the Imhoff system is partial.

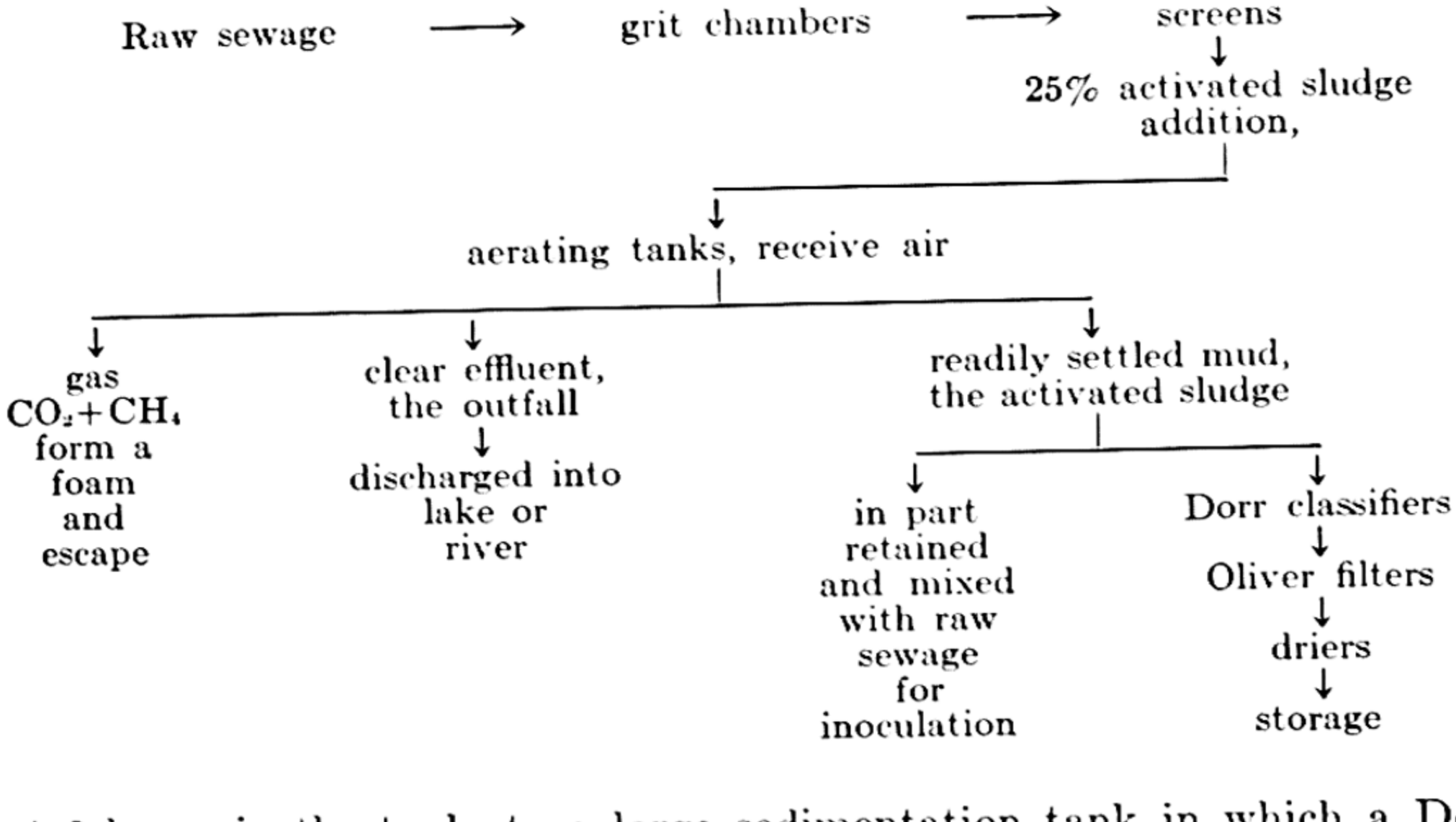
A description of the Milwaukee disposal plant will permit the tracing of the sewage through the plant. (*See* Flow-Sheet page 273.) The raw sewage passes through grit chambers, then through fine screens, to reach an overflow chamber leading to the mixing channel. Here 25 per cent conditioned sludge enters and joins the raw sewage; this is now mixed sewage.

Filtered air is blown in, and the aerated mixed sewage passes to one of

[18] From a private communication from Dr. H. W. Clark, Chief Chemist, Mass. Dept. Public Health, to whom the observations are due.

12 double aeration chambers, open tanks 250 feet long by 85 feet wide. The mixed liquor is 15 feet in depth, and continues to receive air through diffuser plates located in the bottoms of the tanks. The volume of air blown in is just sufficient to maintain the zoogleal [18a] floc in suspension and to furnish sufficient oxygen to supply the microbial organisms in their processes of consuming organic matter and converting it to inert carbon dioxide and water. Each aeration tank delivers its charge, after any one part of it has

Simple Flow Sheet for the Activated Sludge Process of Sewage Disposal (Milwaukee).



spent 6 hours in the tank, to a large sedimentation tank in which a Dorr classifier works; the clear, slightly colored effluent passes out to the lake through a conduit called the outfall. Continuously also the classified mud is pumped in slurry form to a battery of 24 Oliver continuous filters with 14-foot drums, where it is dewatered. Automatic conveyers deliver the moist mud to rotary driers, which it leaves ready for packing. It is used as fertilizer under the name Milorganite, which analyzes 6 to 7 per cent nitrogen as NH_3, and 2 per cent available phosphoric acid.

A portion of the sludge is conditioned by additional aeration, and is used to inoculate the raw sewage.

The plant treats on the average 85 million gallons per day of a strong industrial sewage averaging close to 300 ppm. suspended solids.

A study [19] of the conditions necessary for the clarification of sewage as obtained in the activated sludge process indicates that there must be (1) aerobic bacterial life, (2) protozoa, and (3) oxygen in solution. The protozoa are living organisms, among which there may be mentioned the Vorticella, which is attached to a sludge particle by a stem. (*See* Figure 107).

The process of clarification from the colloidal standpoint consists partly in the assimilation of matter in the colloidal state (albumen, mucin, pro-

[18a] Floc of microorganisms and organic debris.

[19] "The role of protozoa in activated sludge," Robert Cramer, *Ind. Eng. Chem.*, 23, 309 (1931).

tein, algal matter) and of organic bodies dissolved by the protozoa and bacteria, and partly in their oxidation, due also to the presence and activity of the organisms. Because of the colloidally protective function of albuminous matter and of dissolved organic substances on the suspended solids, the destruction of a small amount of the protectants permits the ready settling of a relatively large amount of solids.

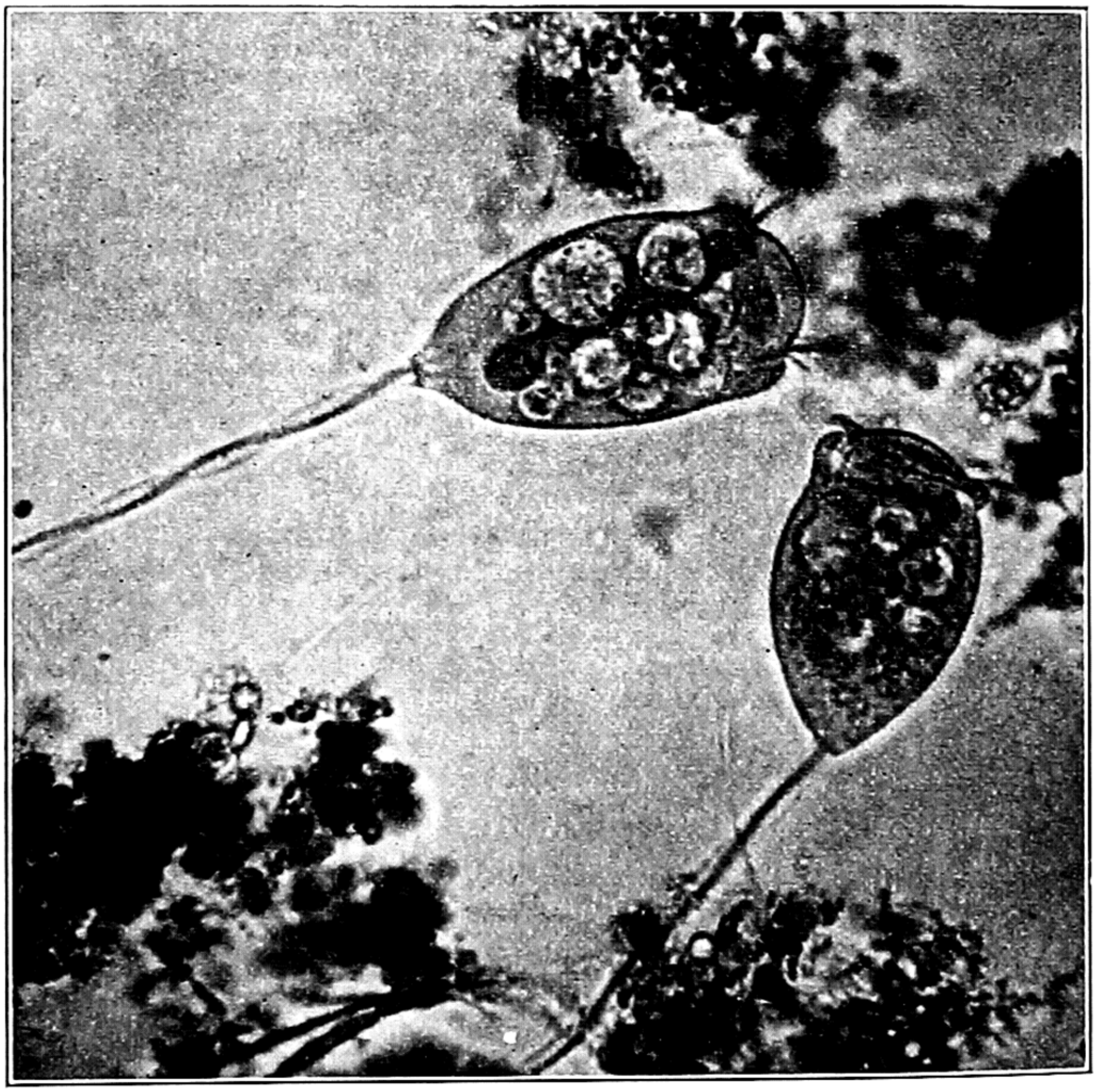


FIGURE 107.—Vorticella attached to sludge particles (400×); one of the protozoa in activated sludge. (Courtesy of Mr. Robert Cramer, Consulting Engineer, Milwaukee, Wis.)

Industrial Waste Treatment. The growing use of water in industry and the growing interest of the public and the government in the abatement of stream pollution have been the important factors in the development of waste treatment by industry. A third but lesser factor has been the belated recognition by industry of the economic possibilities of recovery of valuable by-products formerly wasted. Even this recognition followed work by the sanitary engineers and chemists working in the fields of domestic waste treatment. One of the most outstanding examples is the recovery at a good profit of cattle and chicken feed from distillery slops. On the other hand

the steel industry has not yet discovered an economically feasible method for treating pickle liquor waste, although thousands of tons of acid and iron are lost annually.

It is now a recognized tenet of industrial production that waste treatment is a legitimate cost of production whether or not it returns a profitable by-product. Various industries have attacked the problem of waste treatment through industry-wide associations; most notable of these are the American Iron and Steel Institute, the Pulp and Paper Industry, and the National Canners Association.

Methods of treatment of industrial wastes vary for different types of wastes. Where organic wastes are present but not susceptible to economic recovery, the biological methods of sewage treatment may be employed, including digestion to produce methane and carbon dioxide. Toxic substances may be precipitated by chemical treatment including chlorination. Bottling up of wastes by recycling waters has been feasible in many instances. Another attack on the problem of industrial wastes is to treat the waste in the municipal sewage treatment works and charge the industry for its share of the cost of treatment.[20]

Other Patents

1,515,007 and 1,586,764, on the formation of zeolite mass; 1,820,978, digestion of coarse substance left on sewage screen; 1,820,977, complete sewage treatment plant with submerged aerators; 1,820,976, using activated sludge to prevent acid fermentation; 1,722,945, acceleration of sludge digestion by allowing it to settle and then raising the heavy parts and allowing it to settle a second time; 1,790,975, treatment of sewage by the activated sludge process; 1,779,810, a method and plant for the drying of sewage sludge; 1,642,206, apparatus for the treatment of sewage by the activated sludge process; 1,690,682, keeping the hard, floating sludge submerged by inserting a cover in the digestion chamber; 1,696,846, sewage treatment with a screen acting like a filter; 1,700,722, sewage treatment by activated sludge in combination with a preliminary tank treatment; 2,226,134 and 2,222,559, on purifying or treating water; 2,247,762, same; 2,374,772, sewage aerator; 2,391,951, water softening material made from coffee grounds; U. S. Re-issue 22,652 of Pat. 2,340,842, two-stage plant for treating impure liquids, such as sewage, as in trickling filter plants.

Problems

1. Filter alum, commercial aluminum sulfate, with 16 per cent Al_2O_3 content, is added to a municipal water supply at the rate of 62 pounds per million gallons. The daily volume pumped is 190 million gallons. The alkalinity is sufficient to precipitate all of the aluminum in the form of its hydrate. How much filter alum is added per day, what is the weight of the alum floc formed (on dry basis)?

2. If the alum used in Problem 1 had to be precipitated by soda ash, 98 per cent pure, how much soda ash per day would be required?

3. The chlorine is added to a municipal water at the rate of 2 pounds per million gallons. Over the year, with chlorine 2 cents a pound, how great is the expenditure for this item, if the daily output is 130 million gallons?

4. If 100.000 grams of raw water, containing $MgCl_2$ equivalent to 239 ppm of $CaCO_3$ were passed through a zeolite ion exchanger system, what weight of salt (NaCl) would be required for regeneration of the sodium zeolite? Provide a 150 per cent excess of salt in the regeneration.

[20] "Special Sewer Service Charges for Industrial Wastes," George E. Symons and Frederick W. Crane, *Water Works & Sewerage*, 91, p. R-166 (June, 1944).

Reading References

"Public water supplies," 4th Ed., F. E. Turneaure and H. L. Russell, New York, John Wiley and Sons, Inc., 1940.

"Industrial water supplies, requirements, development and design," Sheppard T. Powell and Hilary E. Bacon, *Ind. Eng. Chem.*, 29, 615 (1937).

"Ferric alumina, a modern development in the field of coagulation," A. R. Moberg and E. M. Partridge, *Ind. Eng. Chem.*, 22, 163 (1930); U. S. Patent 1,679,777.

"Sodium aluminate in modern water treatment," R. B. Beal and S. Stevens, *J. Soc. Chem. Ind.*, 50, 307T (1931).

"Zeolite softening of lime-treated water at Columbus, Ohio, water softening and purification plant," C. P. Hoover, V. L. Hansley and C. Q. Sheely, *Ind. Eng. Chem.*, 20, 1102 (1928).

"Water treatment and purification," 2nd Ed., William J. Ryan, New York, McGraw-Hill Book Company, 1946.

"Studies on the nature and amount of the colloids present in sewage. Part VII. The effect of bubbles of gas and agitation on sewage liquors," E. Williams, *J. Soc. Chem. Ind.*, 54, 355T (1935).

"The activated sludge process, Withington works," Edward Ardern and William T. Lockett, *J. Soc. Chem. Ind.*, 42, 225T (1923).

"Phosphates in water conditioning," Charles Schwartz and C. J. Munter, *Ind. Eng. Chem.*, 34, 32 (1942).

"Sewage treatment at Buffalo, New York," G. E. Symons, C. R. Velzy and Burrows Morey, *Trans. Am. Inst. Chem. Eng.*, 36, 325 (1940).

"Synthetic-resin ion exchangers in water purification, operating characteristics," Robert J. Myers and John W. Eastes, *Ind. Eng. Chem.*, 33, 1203 (1941).

"The absorptive properties of synthetic resins, Part I," B. A. Adams and E. L. Holmes, *J. Soc. Chem. Ind.*, 54, 1-6T (1935).

"Concentration of dilute solutions of electrolytes by base-exchange materials," Roy H. Beaton and Clifford C. Furnas, *Ind. Eng. Chem.*, 33, 1500 (1941).

"Modern Practices in Municipal Water Softening," S. B. Applebaum, *Water and Sewerage Works*, 94, R-141 (1947).

"Ground water, its development, uses and conservation," E. W. Bennison, Edward E. Johnson, Inc., St. Paul, Minn., 1947.

"Review of progress of breakpoint chlorination," A. E. Griffin, *J.N.E.W.W.A.*, 61, 145 (1947).

"Diesel and gas engine equipment," A. M. Boehm, *Water and Sewerage Works*, 94, 379 (1947).

"Dosage control in sewage chlorination," George E. Symons, *Water and Sewerage Works*, 94, R-243 (1947).

"Sewage treatment," Karl Imhoff and G. M. Fair, John Wiley and Sons, New York, 1940.

"Sewerage and Sewage Treatment," 6th Ed., Harold E. Babbitt, John Wiley and Sons, New York, 1947.

"Sewage gas engine supply power for disposal plant at Durham, N. C.," Milton F. Merl, *Southern Power J.*, 54, No. 12, 50 (1936).

"Sewage treatment processes and results," George E. Symons, *Water Works and Sewerage*, 91, R-175 (1944).

"Activated sludge bulking," L. H. Enslow, *Water and Sewerage Works*, 93, R-225 (1946).

"Symposium on industrial waste treatment, *Ind. Eng. Chem.*, 39, 559 (1947).

"Activated silica, a new chemical engineering tool," Reynold C. Merrill and Harry L. Bolton, *Chem. Eng. Progress*, 1, 27-32 (1947).

"Ion-exchange demineralizing of solutions," F. R. Riley and H. M. Day, *Chem. Eng. Progress*, 44, 353 (1948).

"Silica removal by an improved ion-exchange process," V. L. Calise and M. Lane, *Chem. Eng. Progress*, 44, 269 (1948).

"Accelerated waste treatment methods," E. G. Kominek, *Chem. Eng. Progress*, 45, 417 (1949).

Until recently, the possession of coal fields was needed to insure security and industrial prosperity to a nation; with the advances in water-power utilization and the discovery of petroleum in certain coal-poor countries, a partial independence of coal has resulted. The petroleum-poor countries can help themselves by making motor spirits from coal, by hydrogenation, or by the Fischer-Tropsch synthesis—a state of affairs which favors the coal-rich countries again. Benzene production still depends upon coal distillation, although toluene production does so no longer. Ammonia had its main source in coal, until the advent of synthetic ammonia made from atmospheric nitrogen, a store available to all. Modern science offers compensations to nations not favored by a full list of natural resources.

Chapter 14

The Distillation of Coal for Gas, Coke, Tar and Ammonia

The chief use of coal is as a fuel, as described in Chapter 12; but more efficient use (economically) can be made of this material, or at least certain grades of it, by separating from it those portions which may be used in other, more specific processes, and burning only that portion of the coal which cannot be so used. Also, it may be transformed into other forms of fuel, more valuable merely because of their greater convenience of application and transportation. The processes used are all destructive distillations, performed in the absence of air.

Coke which is made from the proper mixture of coals and heated long enough is a hard, strong material, the "metallurgical coke" used in blast furnaces. It is made by distilling, or coking, bituminous coal, in beehive ovens, in retorts, or in the by-product coke ovens of more recent development. In 1944, in the midst of World War II, there were produced 74,037,817 tons of coke, valued at $7.12 a ton. In 1945, the production of coke was 67,308,181 tons, valued at $7.55 a ton; the coal charged to ovens in the same year was 95,348,792 tons, valued at $5.13 a ton. In 1946, the coke production was less, corresponding to the lesser tonnage (83,288,000 tons) of coal charged to ovens. Until 1889, all coke was beehive coke, and only gradually since then has the original 100 per cent decreased as the by-product oven coke became acceptable to the metallurgical trade. In recent years, especially over the period of World War II, beehive coke has again been made in sizable quantities, partly because of the great need for metallurgical coke. The beehive coke, which was 2.61 per cent of the total coke in 1935, rose to 5.3 per cent in 1940, and to 7.75 per cent in 1945.[1]

Of the total 1945 production, 69.5 per cent was used in blast furnaces, as metallurgical coke; the value for the portion sold was $7.48 a ton.[1]

In the beehive process, coke is the sole product; a part of the volatile matter is lost outright; another part serves merely as fuel. In the by-product installations the volatile part is collected; the combustible gas is purified from ammonia, tar, and vapors such as benzene, which are all recovered and utilized. The yield of coke is higher in the modern oven; the

[1] "Minerals Yearbook."

average yield in 1945 was 70.94 per cent of the coal charged, in the by-product oven, and only 64.10 per cent in the beehive; this is a further argument, at least in peace time, against the beehive oven.

In municipal plants, coal is distilled in retorts, primarily for its gas. Originally, the coke produced was dumped onto the grates, to furnish the heat to the retorts above; but today the coke is generally sold for domestic uses, and the heat required for the retorts is obtained by means of producer gas. In modern plants, the retorts are vertical, and circular or rectangular in cross-section.[2] The operation of coking is continuous; coal enters at the top by gravity; coke is withdrawn at the base, periodically, through a water-sealed valve. The Woodall-Duckham vertical continuous retort will serve as an example. It is 25 feet high, about 4 feet by 8 inches at the top, and 4 feet by 20 inches at the base; hence it is a narrow chamber, wider at the base, so that the coke, which works down by its own weight, does not jam against the walls. It is built of silica bricks, and is heated by burning producer gas with preheated air in flues provided in the wall. The temperature at the wall is 2500° F. (1371° C.), while the temperature of the coke itself is 1300-1400° F. (704-760° C.). The through-put of coal is 7½ tons per day. Steam (10 per cent by weight based on the coal) is blown into the retort at a constant rate, so that a mixture of water gas and coal gas is the product. Per ton of coal, about 12,500 cu. ft. of gas are collected. Four retorts form a bench; 5 benches on each side of an aisle form an average unit.

The coke is worked out by a slow-moving helical grate, and reaches a quenching box, from which it is discharged by a hand-operated semi-barrel valve.

The gas is purified from tar and ammonia, which are recovered, so that the plants belong to the by-product class. For small installations, they are very satisfactory; for large cities, the by-product coke ovens such as the Otto, Semet-Solvay, and Koppers are more economical, in spite of a higher first cost.

By-product Coke Ovens

For modern plants of large capacity, the oven is a narrow vertical chamber with silica-brick walls; the chamber is 28 to 39 feet long, 14 feet high, and has an average width of 14 to 18 inches. It is wider at one end (19 inches) than at the other (17 inches), in order to prevent jamming of the coke when discharging. Heat is supplied by burning gas on the outer side of the chamber walls. A number of ovens (such as 60) form a block; the operation is intermittent per oven, but continuous for the block. The period of heating varies; an average is 17 hours.[3] The temperature in the flues, that is, at the outer side of the chamber wall, lies between 2150° and 2550° F. (1177° and 1400° C.); the temperature of the coal within the chamber is less, perhaps 1800° F. as maximum (982° C.) would be a fair average. These are the temperatures found in general practice, which is

[2] The Glover and West, and the Woodall-Duckham.

[3] Coke oven engineers speak of "inch-hours," obtained by dividing the period of coking in hours by the width of the oven in inches; hence it is the number of hours per inch. The effort is to reduce it.

termed high-temperature carbonization, in contrast to many proposals for working at lower temperatures, referred to as low-temperature carbonization processes; these are discussed briefly further on. Generally the air for combustion is preheated, the gas is not. The outgoing gases furnish heat to regenerating chambers, of which there are, in one type of construction, two per oven. The direction of the air and of the fire gases is reversed every 15 or 20 minutes; a scheme for reversing is illustrated in Chapter 11. At the end of the distillation period, the red-hot mass of coke is pushed out of the oven in a single stroke of a ram, in the short space of 3 minutes; the ovens

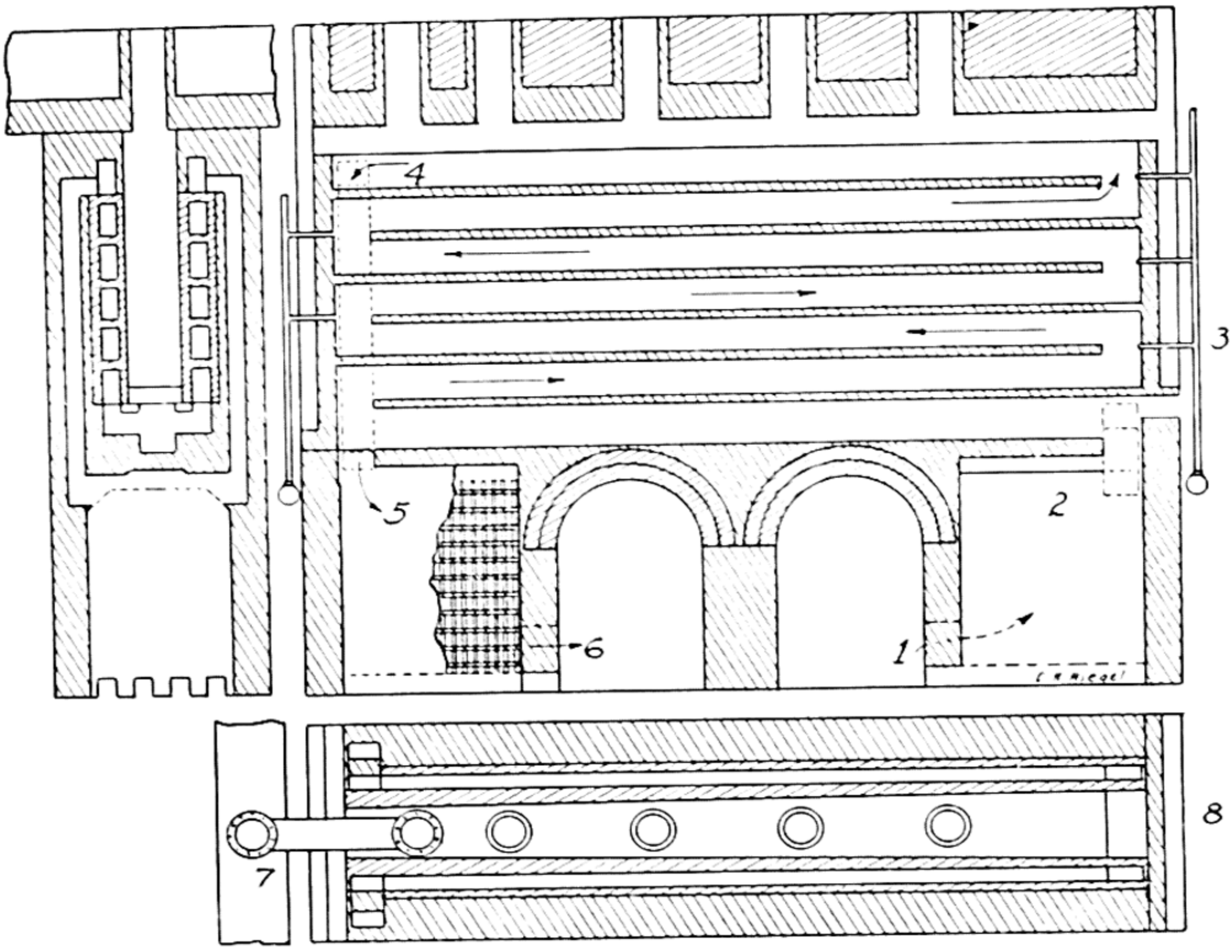


FIGURE 108.—*Upper right*, vertical cross-section, lengthwise, through the Semet-Solvay by-product coke oven, showing the heating flues. Air from tunnel 1 enters the hot checkerwork in regenerator 2, and passes along the flues and upward, burning the gas which enters through burners 3; the fire gases descend at 4 through a vertical channel to regenerator 5, and to the stack through tunnel 6. *Upper left*, vertical cross-section, crosswise, showing flues and oven proper. *Lower right*, horizontal cross-section showing width of the flues and taper of oven, also the four charging holes and the hydraulic main connection at 7; the ram enters under 7, the coke drops off at 8. For dimensions, *see* text.

are elevated so that the coke may be made to fall into a special car on railway tracks. The car is pulled to the quench hood, and there quenched by water. It is then dumped onto a sloping platform which leads to belt conveyors; these bring the coke to screens, chutes, and railway cars for shipment. The oven charge is 11 tons of coal, or more.

In the arch forming the roof of the oven, 4 charging holes are pro-

vided, with a fifth opening for the escape of the gases; the latter opening carries a cast-iron goose-neck, which reaches into a horizontal steel trough running the length of the block, the "hydraulic main." The gas from all ovens is collected in this main and conveyed by extensions to the coolers, purifiers, and meters; the liquid in the main (tar), overlaid by an impure

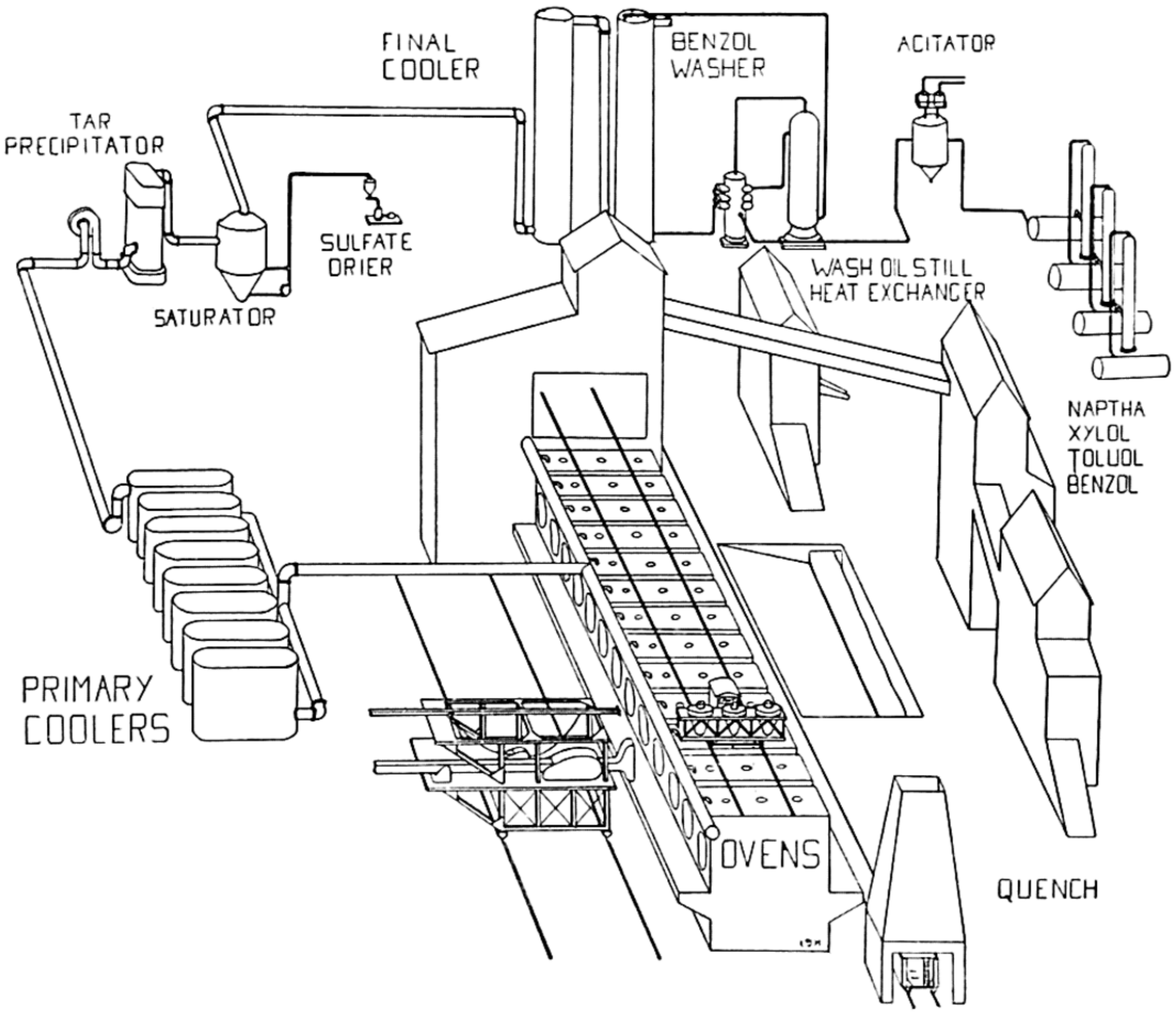


FIGURE 109.—A pictorial flow sheet of the by-product coke oven installation for the distillation of coal. The several parts will be identified by the legends, and by the statements in the text. (Sketch by Joseph Magee.)

ammoniacal water solution, serves as a seal to each retort, so that while one is being discharged, the gas does not escape, nor does air enter. The front and back of the oven are closed by cast-iron doors lined with silica bricks. When reset after discharge, the doors are luted with mud to make them gas-tight.

The coal is charged from a special car traveling on tracks laid on the roof of the ovens. The coal is carefully chosen; nearly always a mixture of two or more kinds is used, to obtain a coke which will be suitable for metallurgical purposes. The mixture may be 20 per cent of a low-volatile coal (16-18 per cent volatiles), and the rest a higher-volatile coal (30-35 per cent volatiles) with coking properties. The coal is crushed by rolls fol-

lowed by a swing-hammer mill;[4] it is conveyed to a bin sufficiently elevated so that the traveling charging car may be loaded by gravity.

Dry Quenching of Coke. The heat in the coke and hot gases represents 70 per cent of the applied heat. When the hot coke is quenched with a stream of water, as is the custom, its sensible heat is wasted. Attempts have been made to substitute "dry quenching," by circulating an inert gas over the coke and under a boiler; in one trial which has been reported,[5] a recovery of 70 to 75 per cent was made.

Cooling and Purifying the Gas. Assuming that the gas is to be sold to a municipality, it must pass certain tests of purity, and on burning must furnish 537 Btu.[6] per cubic foot. Formerly a candle-power requirement was also made, usually 18 candle power; the tendency is to abolish it because the gas flame alone is now rarely used for light. The purification leads to the collection of the by-products, tar and ammonia. The appreciable content of benzene and homologs would not need to be removed, but since the purpose of these ovens is to provide by-products, they are scrubbed out of the gas by oil. The removal of benzene lowers the candle power, but as this requirement is gradually disappearing, the gas remains salable. There is left in the gas a hydrogen sulfide impurity, which is removed by contact with wood shavings coated with lime and iron oxides, or by "liquid purification."

Coolers. The gas leaves the oven at rather moderate temperatures, for the greater part is evolved in the early stages of the coking. Some cooling takes place in the hydraulic main and its extensions leading to the cooler proper, so that it generally reaches the latter with a temperature of 170° F. (77° C.). The coolers consist of steel towers, with wooden grids; the gas comes into direct contact with the cooling liquid, a solution of ammonia, which is itself cooled in pipes sprayed with water and recirculated. A gain in liquor occurs, for the gas holds less moisture cold than hot; this excess is sent to the ammonia still. The cooled gas is drawn by centrifugal exhausters from the cooler and pressed (warmed somewhat by the compression) past the baffles of a tar extraction box into the ammonia scrubbers.

Ammonia Extraction. *a. By scrubbers.* The gas rises in a steel box filled with grids, meeting a descending stream of weak ammonia liquor; from the first box it reaches a second, and a third, fourth and fifth, losing its ammonia. The liquor from the first tower (with respect to gas travel) is the strongest solution of ammonia; the fifth tower receives water, and its liquor is fed to the iourth tower, and so on. The cleaned gas passes to the benzene scrubbers. The ammonia is present in the form of ammonium hydroxide and of ammonium salts, sulfides, carbonates, and others.

b. By direct sulfate formation. This method renders subsequent distillation in a still unnecessary, and is therefore being adopted in all the newer installations. All the gas passes through a sulfuric acid solution,

[4] Chapter 44.

[5] "Dry quenching of coke," D. W. Wilson, *Proc. Intern. Conf. Bituminous Coal, 2nd Conf.*, Pittsburgh, Pa., **2**, 685 (1928).

[6] New York State Public Service Commission standard, unless the state sets a different specification.

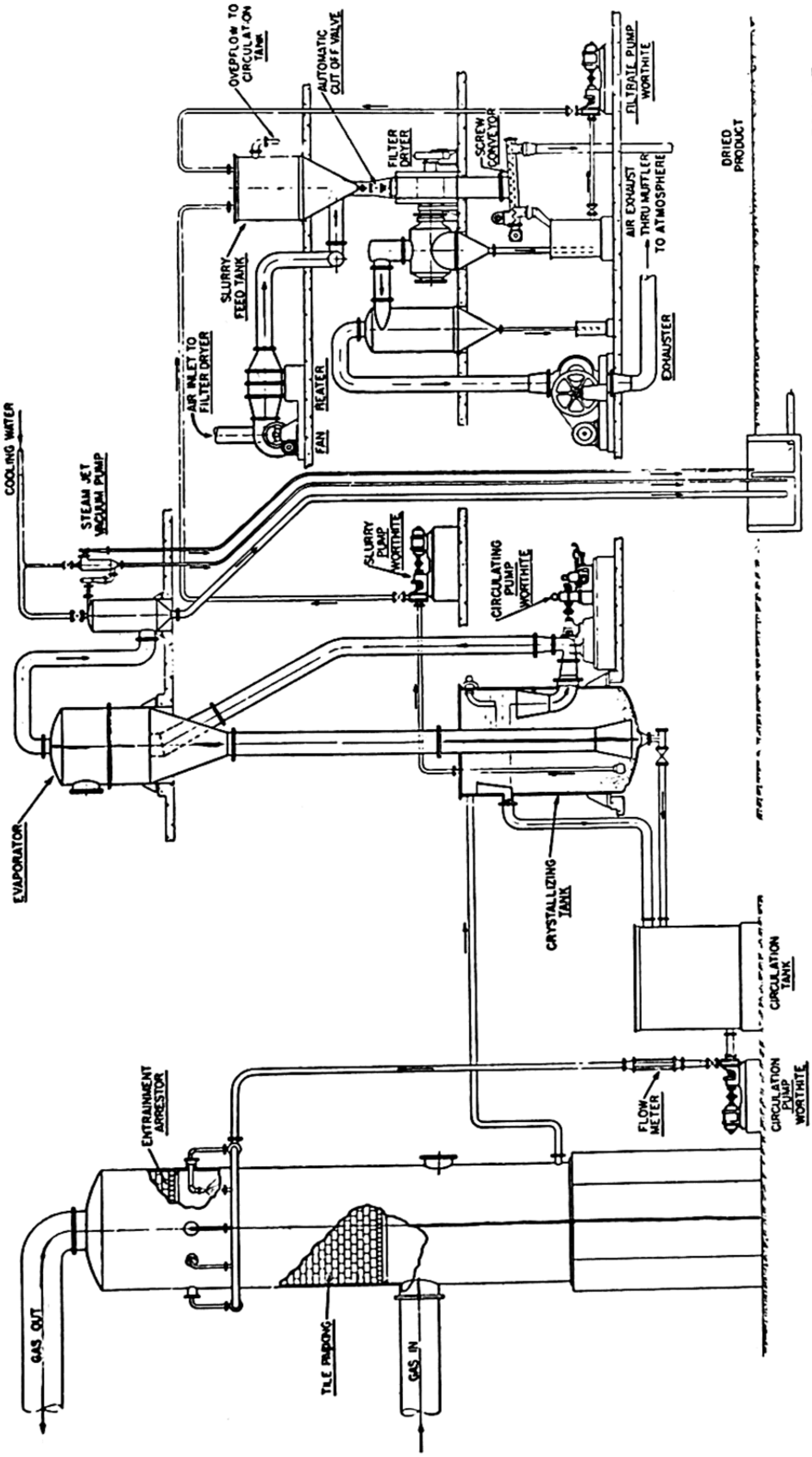


FIGURE 110.—Sketch illustrating the Wilputte ammonium sulfate crystal process. (Courtesy of Worthington Pump and Machinery Corporation, Harrison, N. J.)

where the ammonia is retained and precipitated as ammonium sulfate. The slurry is continually pumped out (by a small steam-jet pump), the salt centrifuged, and the mother liquor returned to the absorption box with additional sulfuric acid.

The several systems are all continuous and automatic. In the Koppers system, the coke-oven gas, after a final purification in an electrical precipitator, enters the saturator directly, bubbling into 4 inches of the acid liquor, and meeting the fresh acid on its way out. In another system, the coke-oven gas need overcome no head of liquid, but is delivered to a rain of droplets of the acid liquor in the saturator. In the Wilputte system, the coke-oven gas rises through a packed tower, which interposes but slight resistance, and down which the acid liquor travels.

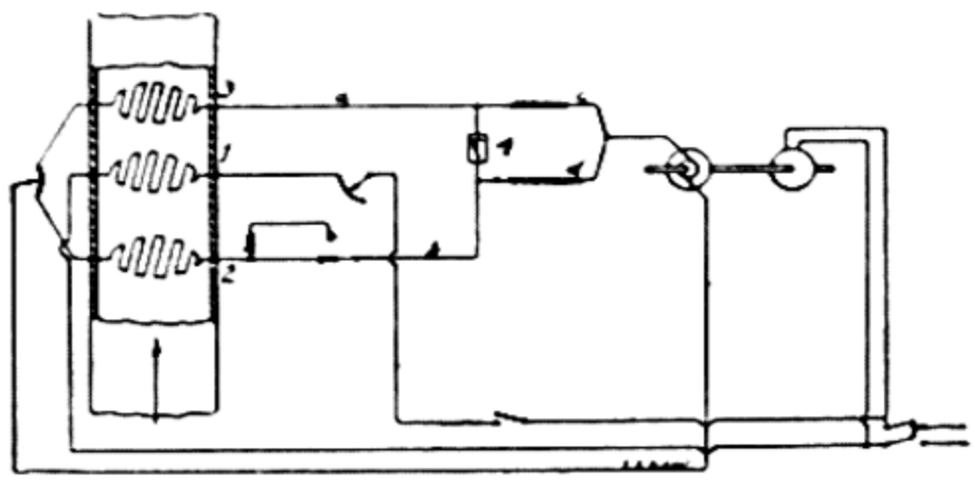


FIGURE 111.—The Thomas meter for measuring the volume of gas flow; 1, heating coil; 2, thermometer for entering gas; 3, thermometer for outgoing gas; 4, galvanometer in the Wheatstone bridge *abcd*.

Benzene Recovery. After losing its ammonia, the gas travels upward through tall steel towers packed with grids or other packing, meeting a stream of "straw oil" which takes up the benzene and toluene from the gas. The charged oil is distilled; the light oil, benzene and toluene are collected and refined further to salable grades, and the free oil used over again. As a rule, two towers work in series.

Purifying Boxes. The gas is next purified of its sulfur content, in one of the modern liquid purification systems, described further on, less frequently by means of the purifying boxes filled with wood shavings impregnated with iron oxide and lime. The packing retains hydrogen sulfide. After a period, the activity decreases, and the mass must be exposed to the air, to be revivified. It may then be used over again. A certain number of such exposures cause an accumulation of sulfur, and the mass may be used as a source of sulfur for sulfuric acid manufacture, in chamber sets.[7]

The Thomas Meter. There remain now only the metering of the finished gas and the testing of its heat value. One device for metering is the Thomas meter (Figure 111) in which a measured quantity of electrical current, sent into a resistance-wire heating coil, is so varied that a differential of 2° F. is maintained between the temperatures of the entering gas and the gas which has passed the coil. It is the variation in this heating current which forms the basis of the measurement. The temperatures of the gas affect the resistance of two nickel wire grids which form part of a Wheatstone bridge. With standard heating current and standard flow of gas, their resistance ratio is definite; any change in the flow dis-

[7] The mass is burned and the sulfur dioxide sent to chambers; carbon dioxide is evolved in the burning also, and tends to render the operation of the chamber very difficult.

turbs the balance, and more or less current enters the heating grid by the aid of a small motor-driven regulator. The instrument is automatic and recording, and is graduated to read cubic feet direct.[8]

Volumetric meters are being installed more and more; one of them is the Connersville meter, which is the reverse of the Connersville blower: the traveling gas drives the impellers, whose revolutions are recorded on a counter, thus giving a measure of the flow.

The Thomas Calorimeter. The heat content of the gas is measured continuously by the Thomas calorimeter, and the readings are recorded automatically on a chart indicating Btu. per cubic foot.[8]

Yield. The amounts of gas, coke, and other materials obtained from 1 ton of coal vary with the kind of coal used; as a guide, the following figures may be given:

1 ton of coal produces 10,000 to 11,000 cubic feet of gas
1400 to 1500 pounds of coke
10 gallons of tar
18 to 30 pounds ammonium sulfate
2.7 gallons motor spirits.

In 1940, the figures were: 10,900 cubic feet of gas, 8.79 gallons of tar, 22.00 pounds ammonium sulfate, 2.93 gallons crude light oil. (Bureau of the Census).

A large portion of the tar is obtained from the hydraulic main, the liquid contents of which are allowed to overflow to the decanter, where the tar forms a lower layer, the ammoniacal liquor an upper layer.

In the Koppers oven, the flues in the chamber wall are vertical, and connected by cross-over channels to the flues in the opposite wall, where the fire gases descend and pass out to a regenerator. (*See* Figure 112.) Other ovens are the Otto, the Wilputte, Foundation, Piette, and Roberts.

The combination of a water-gas plant[9] and a coke-oven gas plant is not infrequent; the gases are sometimes mixed, or the water gas may be burned in the flues of the oven, thereby releasing the equivalent volume of coke-oven gas for sale.

The underground gasification of coal has received attention, especially in Russia.[10] One large-scale test has been run in Alabama, under favorable circumstances, with fair results. The coal, *in situ*, is ignited and a limited volume of air is admitted; combustion and distillation take place at the same time. The gases and vapors produced are carried out of the mine by the draft, and collected.

Liquid Purification. A new method of purifying gas is by means of liquids which absorb the impurity, mainly hydrogen sulfide, and later under different conditions, give it up, at the same time regaining their original absorbing power. The new method has taken a number of different forms. In the earliest form, a 2 to 5 per cent solution of sodium carbonate is the

[8] The Cutler-Hammer Manufacturing Company, Milwaukee, Wis., publication T-4. The calorimeter is reproduced in *Ind. Eng. Chem.*, 18, 1088 (1926).

[9] Chapter 15.

[10] "Underground gasification of coal in the U.S.S.R.," N. Beniaminov, *Gas Worlds*, 114, 101 (1941); also in *Mining J. (London)*, 212, 99 (1941); *C.A.*, 34, 1460 and 1461 (1940); and *C.A.*, 30, 1207, for several abstracts (1936).

active agent.[11] The gas passes upward in a tower with wooden grids, and meets the descending sodium carbonate solution. Hydrogen sulfide, carbon dioxide and hydrogen cyanide are retained in the liquor, while the clean gas passes on. The foul liquor is pumped to the top of a second tower, while hot, and meets a blast of air which travels upward, driving out hydrogen

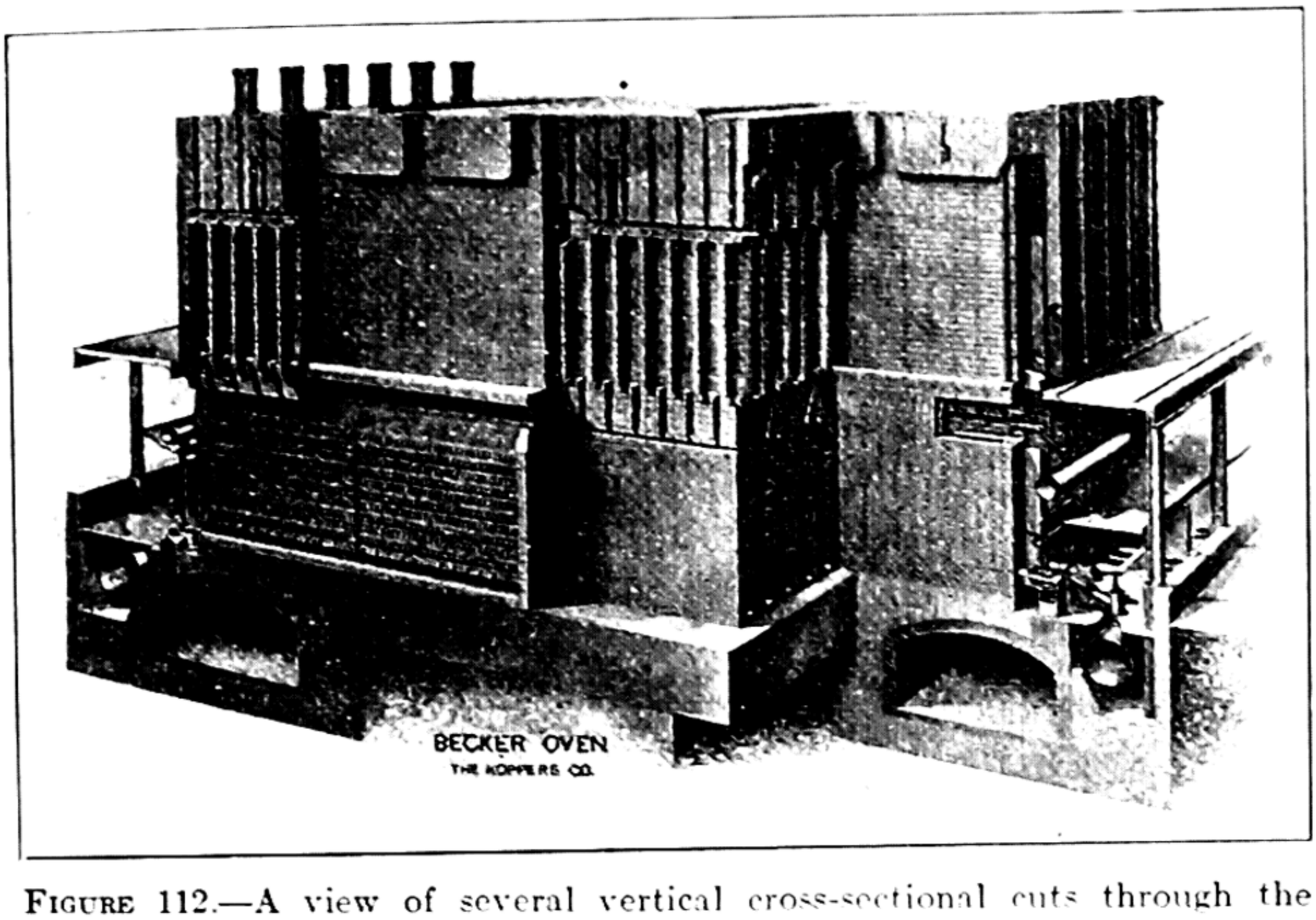


FIGURE 112.—A view of several vertical cross-sectional cuts through the Becker oven, showing: The two arched canals for air; the regenerators; the heating gas lines; the vertical flues with cross-overs; several ovens, and their charging inlets. The heating flames travel up on one side of oven, and down on the other, to enter the regenerator. As shown, the gas is not preheated in the coke oven structure. (Courtesy of the Koppers Construction Co., Pittsburgh, Pa.)

sulfide, hydrogen cyanide, and carbon dioxide. The reactions which take place are given below; they are reversible, and run to the right while the gas passes, but to the left while the air is blown in.

$$Na_2CO_3 + H_2S \rightleftarrows NaSH + NaHCO_3; \quad Na_2CO_3 + CO_2 + H_2O \rightleftarrows 2NaHCO_3;$$
$$Na_2CO_3 + HCN \rightleftarrows NaCN + NaHCO_3.$$

The gases passing out of the liquid purifying agent may be burned under a small fire, to prevent a nuisance.

Other processes employ triethanolamine [12] or sodium phenolate in solution. In the first, cold triethanolamine in solution absorbs the impurities from the coke-oven gas; after it is saturated, it is treated with steam, which restores it to its original state, while the impurities pass out of the

[11] U. S. Patent 1,389,980 and 1,390,037. *See also* the Petit process, in which a solution of potassium carbonate is recommended, and essentially the same reactions take place; described on p. 537, "Modern Gashouse Practice," Alwynne Meade, London, Ernest Benn, Ltd., 1921.

[12] "Organic bases for gas purification," R. R. Bottoms, *Ind. Eng. Chem.*, 23, 501 (1931).

system. In the Koppers phenolate process,[13] the refinery gas or the natural gas rises in the plate column absorber, meeting a descending cold liquid, a solution of phenol in caustic. The clean gas leaves overhead, while the foul solution passes through a heat exchanger and enters the reactivator or actifier, also a plate column, where it meets steam rising from the lowest portions of the solution which lie in contact with a steam chest. The hydrogen sulfide is driven out overhead, and may be burned to produce

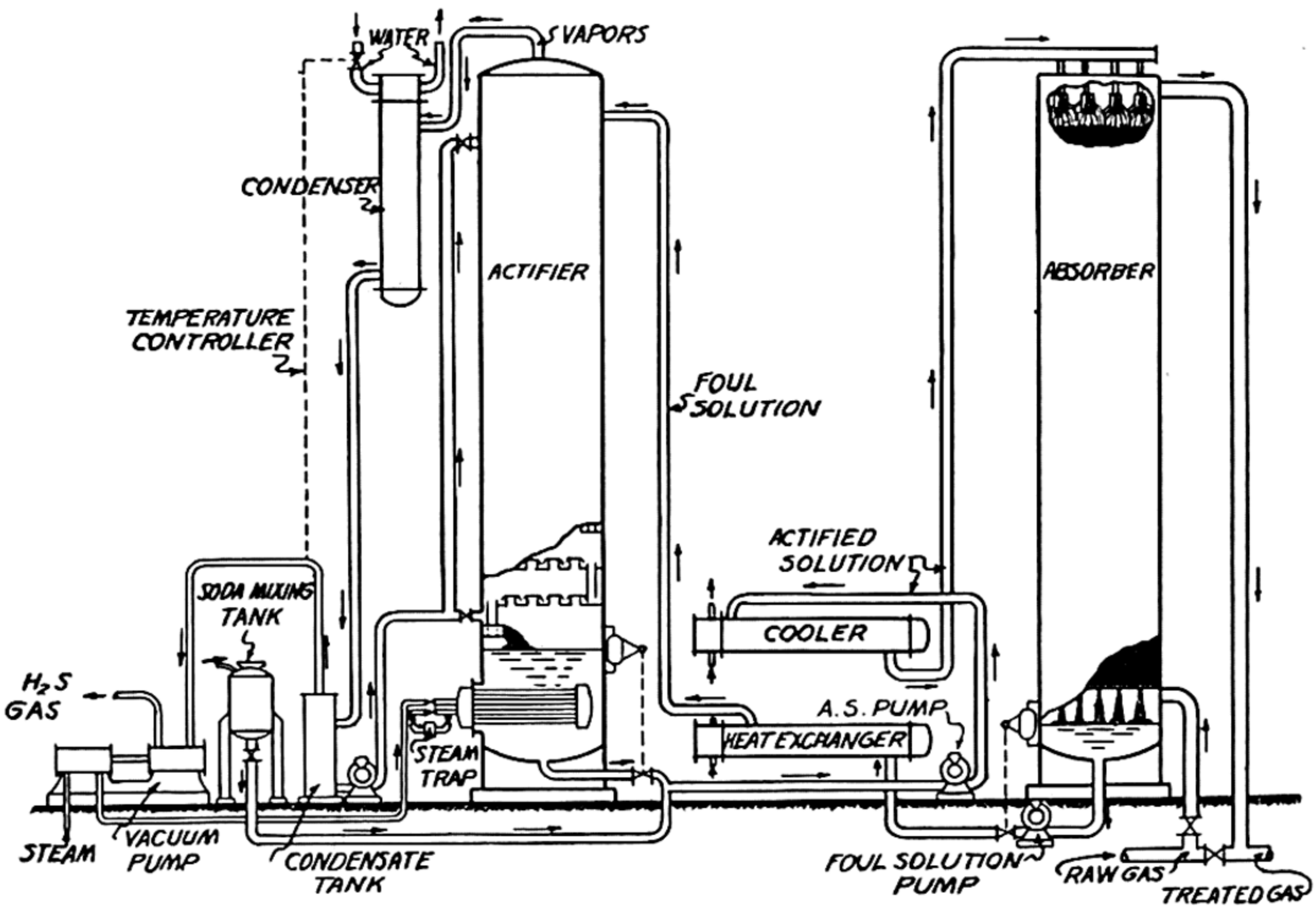


FIGURE 112a.—The Hot Actification sulfur recovery process, for the purification of coke oven gas and similar gas. (Drawn after the sketch furnished by Koppers Company, Pittsburgh.)

sulfur dioxide. The reactivated solution is cooled and used over again. The high carrying capacity of this solution makes it possible to pump only 5 to 10 gallons of solution per 1000 feet of sour gas, a low ratio.

In the Koppers Hot Actification sulfur recovery process, the solution of sodium carbonate is regenerated by boiling the solution under a vacuum.[14] The absorbed impurities, again mainly hydrogen sulfide, are liberated in a concentrated form, and may be conveniently converted into sulfuric acid in amounts generally sufficient for the ammonium sulfate produced in the plant, and for other process requirements. The installation on Neville Island (Pittsburgh), shown in Figure 112a, treats 22,000,000 cubic feet of gas per day, and recovers approximately 7 tons of hydrogen sulfide per day —enough to produce almost 20 tons of 66° Bé. sulfuric acid.

[13] "Koppers phenolate gas purification process for recovery of sulfur from natural and refinery still gases," the Koppers Construction Company, Pittbsurgh, Pa.; also U. S. Patents 1,971,798, 2,002,357, 2,028,124, 2,028,125.

[14] U. S. Patent 2,379,076, June 26, 1945.

The Girbotol process uses triethanolamine, the Shell phosphate process an aqueous solution of tripotassium phosphate (40 to 50 per cent by weight); both remove the sulfur in the form of hydrogen sulfide.

Instead of driving out the gases as such, and either wasting them or recovering them after their combustion, the sulfur may be recovered in the elemental form, by one of several processes, the Thylox, the Ferrox, or the Nickel. The Thylox process [15] uses a solution of sodium thioarsenate, which accepts the sulfur impurity and retains it. In a subsequent step, the loaded solution is blown with air, so that part of the sulfur is liberated and comes to the top of the solution; it is skimmed off and filter-pressed.

$$Na_4As_2S_6O_2 + H_2S \rightarrow Na_4As_2S_6O + H_2O$$
absorbing reaction

$$Na_4As_2S_6O + O \rightarrow Na_4As_2S_6O_2 + S$$
revivifying reaction

In this change due to air, the first compound is reformed, and is ready for new absorption. Sulfur in this extremely finely divided form has proved a valuable fungicide,[16] mainly in the form of a 35 to 50 per cent paste; the 79 per cent material is generally sold as brimstone. In 1944, 19,096 long tons of sulfur were obtained by these processes; the portion shipped was 6,466 tons valued at $40.60 a ton. In 1945, the production was 25,184 long tons (as 100% S).[17]

The recovery in the form of hydrogen sulfide is of similar magnitude; in 1945, the hydrogen sulfide recovered (in 3 states) contained 19,308 long tons of sulfur.[18] Late in 1947, a sulfuric acid plant which will use hydrogen sulfide as its source of sulfur, producing 21,000 tons of sulfuric acid per year, was placed in operation at Kearny, N. J.

Modern Practice in Coal-tar Distillation

In recent years, the distillation of coal tar has received much study and attention, and a number of improvements have been made.

The aim of the tar-distiller is to produce as much oil as possible (from which, then, more of the valuable constituents may be isolated), with a pitch having a high melting point, and at the same time to keep down the formation of free carbon. The higher the temperature, and the longer the tar is subjected to it, the more gas forms, and the less oil. The aims have been therefore to reduce the time of heating, to agitate the tar layers in contact with the heating walls, or to operate in novel ways, avoiding all the old defects. A batch still is a steel vessel heated by an open fire; instead of heating only the lower half, all of it may be heated, reducing the recondensation on the cooler upper walls. The improvements include: modified batch stills, such as vacuum stills, stills with steam agitation, inert gas

[15] "Chemistry of the Thylox purification process," H. A. Gollmar, *Ind. Eng. Chem.*, 26, 130 (1934).
[16] *Ind. Eng. Chem.*, 25, 364 (1933).
[17] "Minerals Yearbook."
[18] In this connection, read: "Cleaning up refinery gases," *Chem. Met. Eng.*, 45, 417 (1938), and "Recovery of sulfur from fuel gases," Alfred R. Powell, *Ind. Eng. Chem.*, 31, 789 (1939).

recirculation, and coke stills, in which the residual pitch is heated until only coke remains [19]; pipe or tube stills, consisting of a coil of pipe set in a furnace, and through which the tar passes continuously; the coke-oven tar still, which is built on top of the coke-ovens, and employs lean coke-oven gas as source of heat.

As the heating of tar progresses, permanent gases are evolved, the free carbon content rises, and the melting point of the resulting pitch increases. The evolution of gases as measured by pressure is shown in Figure 113 [20]; it will be observed that changes are slow below 600° F. (315° C.), and rapid above 700° F. (371° C.). The increase of cracking as the temperature is increased is evident. The free carbon increase is 15 per cent.

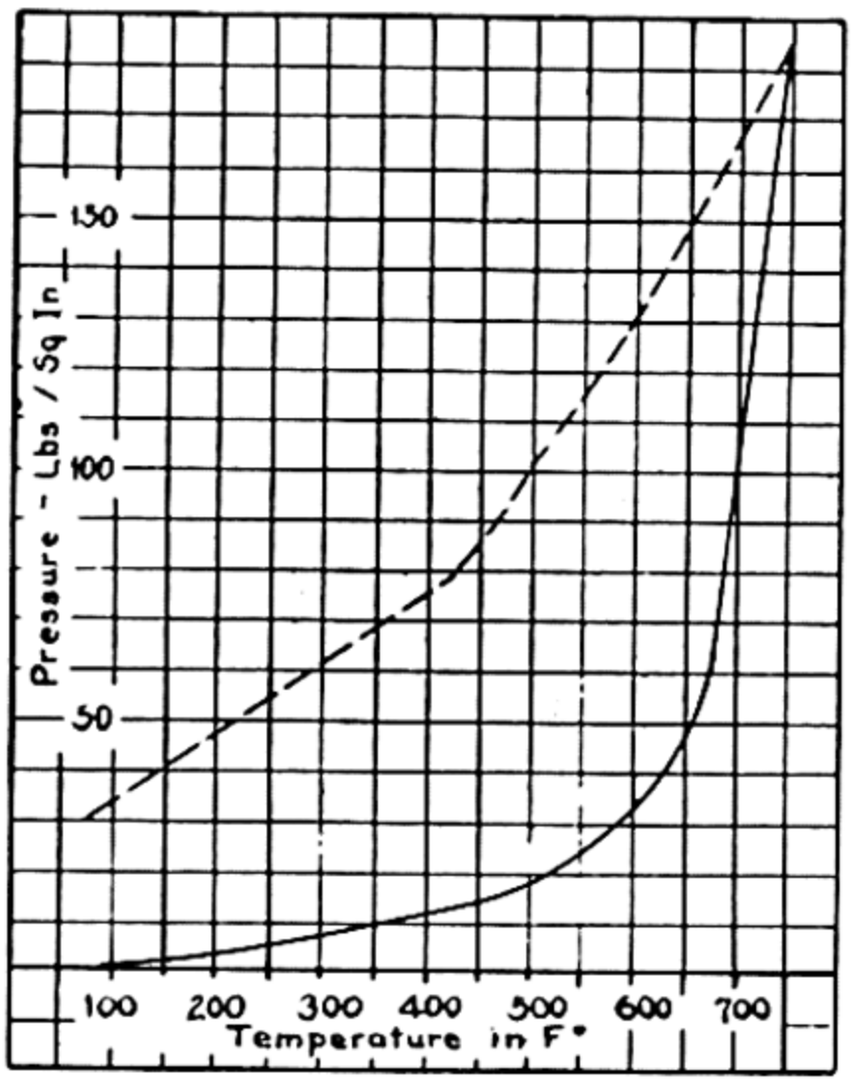


FIGURE 113.—The effect of heat on tar. Full curve, heating tar in autoclave; dotted curve, cooling the same charge in the same autoclave; the higher pressures are due to evolved gases.

The improved recovery of oil in vacuum stills is shown in Table 45.[20]

TABLE 45.—*Vacuum Stills vs. Atmospheric Stills.*

Stills	Temperature ° C.	Temperature ° F.	Oil (Per cent)	Pitch (Per cent)	Free Carbon (Per cent)
Vacuum	330	626	56.6	42.5	28.8
Atmospheric	413	775	40.1	57.8	40.7

In the pitch from the atmospheric distillation the free carbon is 2.8 times that to be expected by the simple concentration of the free carbon present in the original tar; in the vacuum still the increase is 1.4 times. In stills with steam agitation, the improvement is similar.

The inert gas circulation system [21] (*see* Figure 114) has the great advantage of being adaptable to any batch still; the improvement in amount of distillate and, at the same time, higher melting point of resulting pitch are well shown in Figure 115. At first, nitrogen or carbon dioxide was used, and the rate was 0.33 cu. ft. of gas per gallon of tar per minute for carbon dioxide,

[19] U. S. Patent 1,230,782.

[20] "The distillation of coal tar," by John M. Weiss, *J. Soc. Chem. Ind.*, 51, *Chem Ind.*, 10, 219 and 247 (1932).

[21] U. S. Patent 1,418,893; related schemes in U. S. Patent 1,800,224.

and 0.40 cu. ft. per gallon per minute for nitrogen. A sample of the results[20] is shown in Table 46.

It was found that if air is recirculated, its oxygen is soon consumed, and the residual gas is in effect inert. The method has been adapted to stills of capacities varying up to 10,000 gallons.

A recent improvement has been the placing of the distilling vessels on top of the coke-ovens,[22] and utilizing the lean coke-oven gas as a source of heat. Only the sensible heat in such gas is used, and after contact with

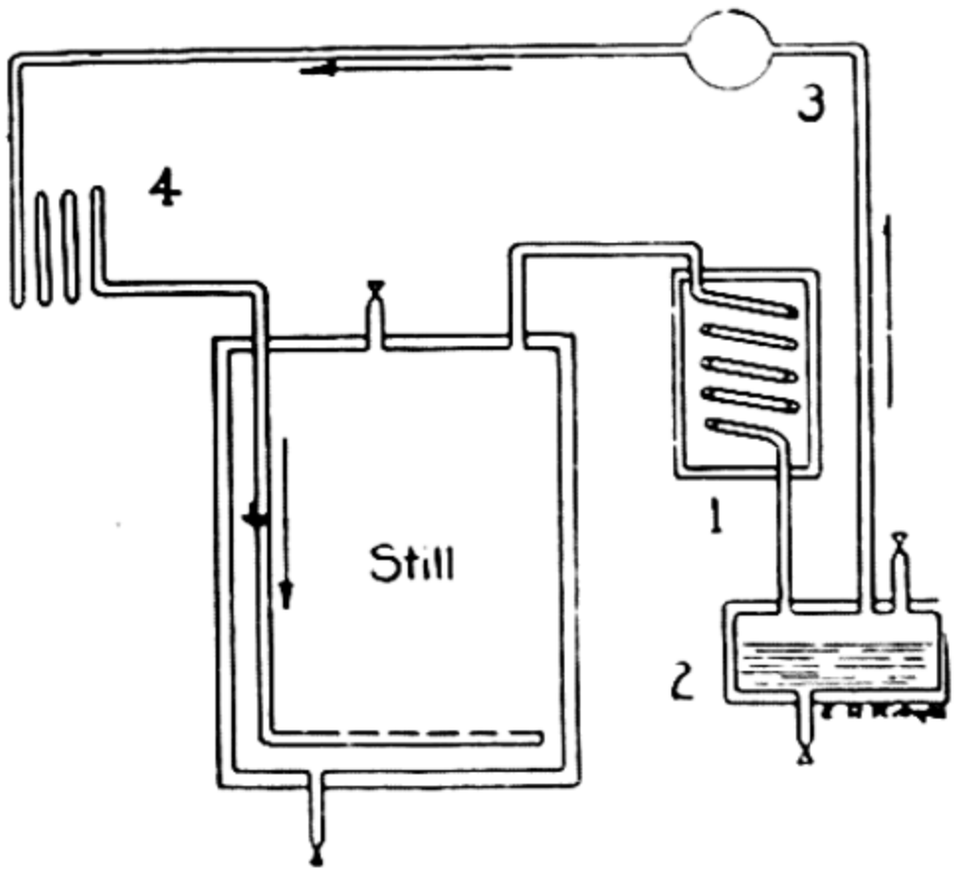


FIGURE 114.—Diagrammatic scheme for the inert gas recirculation process for distilling coal tar. 1, condenser; 2, receiver and separator, the gas passing out to pump 3; 4, heater.

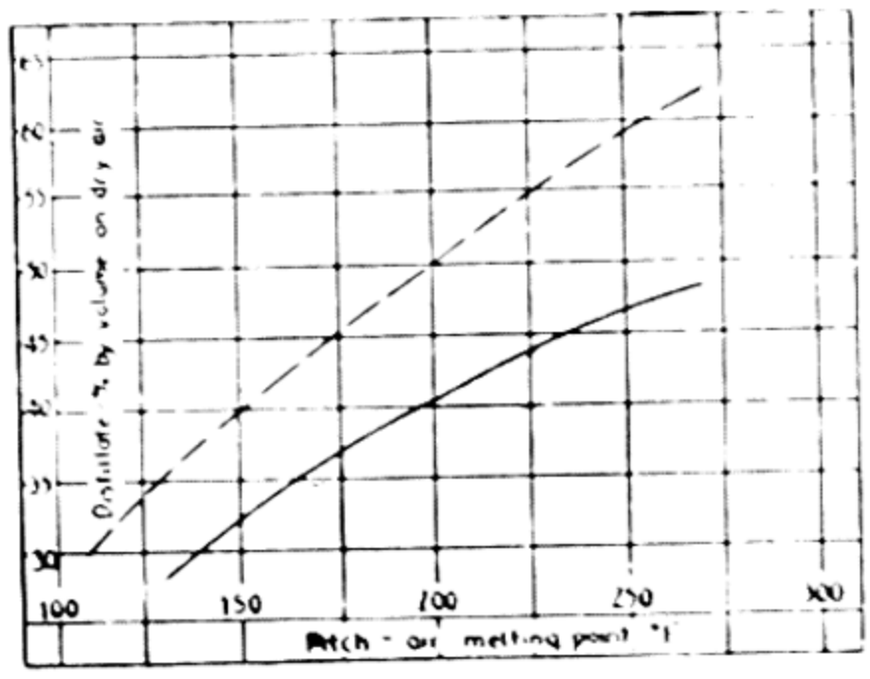


FIGURE 115.—Percentage distillate and corresponding pitch melting point from a tar still with inert gas recirculation (dotted line) compared with ordinary distillation (solid line).

the tar, it rejoins the main flow of gas and yields its combustion heat elsewhere. The cost for fuel is thus nil. Another advantage is that the crude tar need not be transported; any fractions which must be burned are so used on the premises; only the parts for which there are orders are made to bear a shipping charge.

TABLE 46.—*Inert Gas Circulation System vs. Atmospheric Distillation.*

System	Temperature ° C.	Temperature ° F.	Pitch — Per cent	Pitch — M. pt.	Oil — Per cent	Free carbon — Per cent
Atmospheric still	413	775	57.8	280° F. (138° C.)	40.1	40.7
Recirculated CO_2	358	677	46.9	277° F. (136° C.)	52.6	29.0
Recirculated N_2	331	628	46.4		52.0	27.2

The procedure is indicated in Figure 116. The tar is preheated in the coil marked 1, and is delivered in spray form into the distilling tower, passing downward. The hot coke-oven gas passes upward, volatilizing the oils, but allowing the pitch to pass down to the distilling main; in the latter a rotor roll works and splashes the pitch into the incoming gas. Periodically, pitch is withdrawn at 3. The gas leaves the tower laden with oil vapors; it

[22] Can. Patent 304,941 (1930); *see* also 304,940 to 304,946.

deposits the heavy oils while in contact with the coil bringing the new tar. The light oils are recovered in the final tower, packed with rings, down which a cold ammoniacal water solution flows. The condensed light oil and water pass down to a separator, while the cleaned cool coke-oven gas leaves at 5 to join the main flow of gas.

This almost ideal scheme has been quite successful, except that the close control over the quality of pitch which the inert gas recirculation procedure allows is not equaled.

The oil fraction is next divided into four fractions, which contain: (1) the light oil, benzene, toluene, xylene, some pyridine and naphthalene; it forms

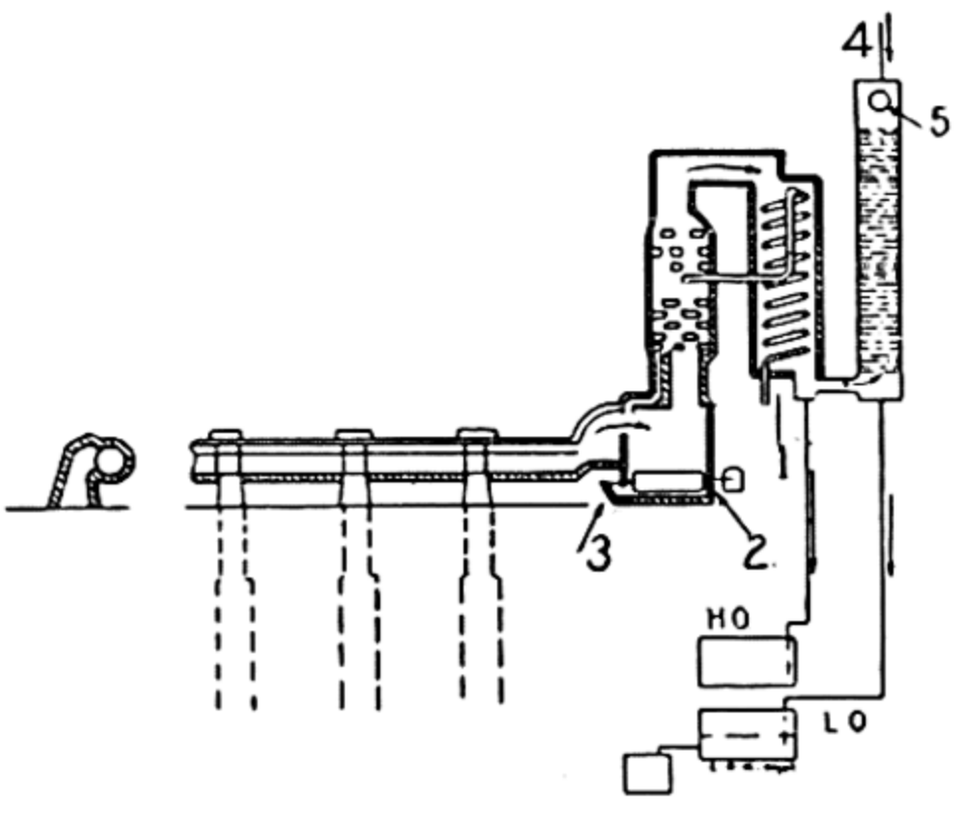


FIGURE 116.—Tar still using the sensible heat of lean coke-oven gas. 1, entry for tar; 2, rotor roll to splash pitch; 3, draw-off for pitch; 4, entry for weak ammonia liquid; 5, outlet for cold gas.

25 per cent of the total, and boils up to 170° C. (338° F.); (2) the carbolic oil, phenol, naphthalene, and pyridine bases; it forms 10 per cent of the total, and boils up to 225° C. (437° F.); (3) the creosote oil, mainly cresols; it forms 10 per cent of the total, and boils up to 270° C. (518° F.); (4) the heavy oil, anthracene, phenanthrene, carbazol, forming 40 per cent of the total, and boiling up to 320° C. (608° F.). The boiling points given are those observed at atmospheric pressure; at reduced pressure, or with inert gas circulation, they are correspondingly reduced.

The refining of these fractions constitutes an important industry, partly because it furnishes the raw materials for dye manufacture, partly because its products are the basis for some of the military explosives which must be obtainable within the borders of the country for the emergency of national defense. The purification is mainly by distillation, caustic treatment, and sulfuric acid washing. The processes are as follows [23]:

(1) The light oil is distilled in fire-heated fractionating stills under reduced pressure; the shelves of the fractionating column have numerous small inverted cones and chimneys so that the rising vapors must bubble through the liquid. The products are crude benzene, crude toluene, crude solvent naphtha, and a residue of tarry nature which serves as fuel.

The various crude products are washed with sulfuric acid, then with caustic solution, and again distilled by themselves in steam-heated stills with columns, at atmospheric pressure. Pure benzene, toluene, and xylene are obtained; per ton of coal, the yield is 0.4 gallon of toluene, 2 gallons of benzene, and 0.2 gallon of xylene.

[23] *Chem. Met. Eng.*, 23, 321 (1920).

(2) The carbolic oil is cooled in large shallow pans, where the naphthalene separates in the solid state; it is centrifuged to form crude naphthalene. The oil which remains is washed with caustic, removing the phenol; then with dilute sulfuric acid, in order to dissolve the pyridine bases; the residue is distilled and gives essentially two parts, solvent naphtha, the distillate, and a resin (coumarone) which is left in the still. The caustic solution is acidified to free the phenol, and the latter is distilled in fire-heated stills at reduced pressure; the product is a crude phenol, which must be redistilled in steam-heated stills. This distilled product is refined still further by mixing it with a little water, cooling it to a cake, crushing this, and

TABLE 47.—*United States production of certain coal-tar crudes (1946).**

			Value per unit
Tar	899,344,000	gal.	
Light Oil and derivatives			
Crude light oil	266,388,000	"	$ 0.08
Benzene, motor grade, tar distillers	4,428,000	"	.117
coke-oven oper.	27,399,000	"	.088
other grades, tar distillers	25,511,000	"	.149
coke-oven oper.	109,729,000	"	.129
Toluene, tar distillers	7,664,000	"	.221
coke-oven operators	16,520,000	"	.205
Xylene, tar distillers	2,135,000	"	.236
coke-oven operators	5,986,000	"	.227
Solvent naphtha, tar distillers	4,475,000	"	.247
coke-oven oper.	4,401,000	"	.129
Pyridine, crude bases	330,000	"	.666
Naphthalene, crude, solidifying below 79° C.			
tar distillers	170,565,000	pounds	.028
coke-oven operators	71,605,000	"	.022
Creosote, oil, total, tar distillers	105,280,000	gal.	.148
coke-oven oper.	31,123,000	"	.142
Sodium phenolate	2,449,000	"	.063
Tar, road	155,525,000	"	.090
for other uses	17,448,000	"	.110
Pitch of tar, soft	303,000	tons	20.304
medium	774,000	"	14.609
hard	694,000	"	14.944

NOTE. Toluene from petroleum, 9,315,000 gal.; xylene, 36,495,000 gal., additional.

* U. S. Tariff Commission.

centrifuging the mass; there is finally obtained the crystallized phenol of commerce.

The pyridine bases are recovered from their acid solution by adding caustic, and then distilled.

The crude naphthalene obtained in the first step is purified by melting, cooling again, and centrifuging the semi-solid mass which results. The cleaned solid in the basket is melted again, distilled in fire-heated stills, and the distillate agitated while melted first with sulfuric acid, then with caustic, and the residue again distilled; the distilled material solidifies on cooling and is the naphthalene of commerce.

Fraction (3) may be used as such.

(4) The heavy oil solidifies on cooling; it is washed with solvent naphtha and filtered; the naphtha contains the phenanthrene. The filter cake is next washed with pyridine, to remove carbazol. The remaining solid is sublimed and condensed in large chambers, as a white solid; it contains 80 to 85 per cent anthracene.

The pyridine solution is distilled, yielding in the distillate first pyridine,

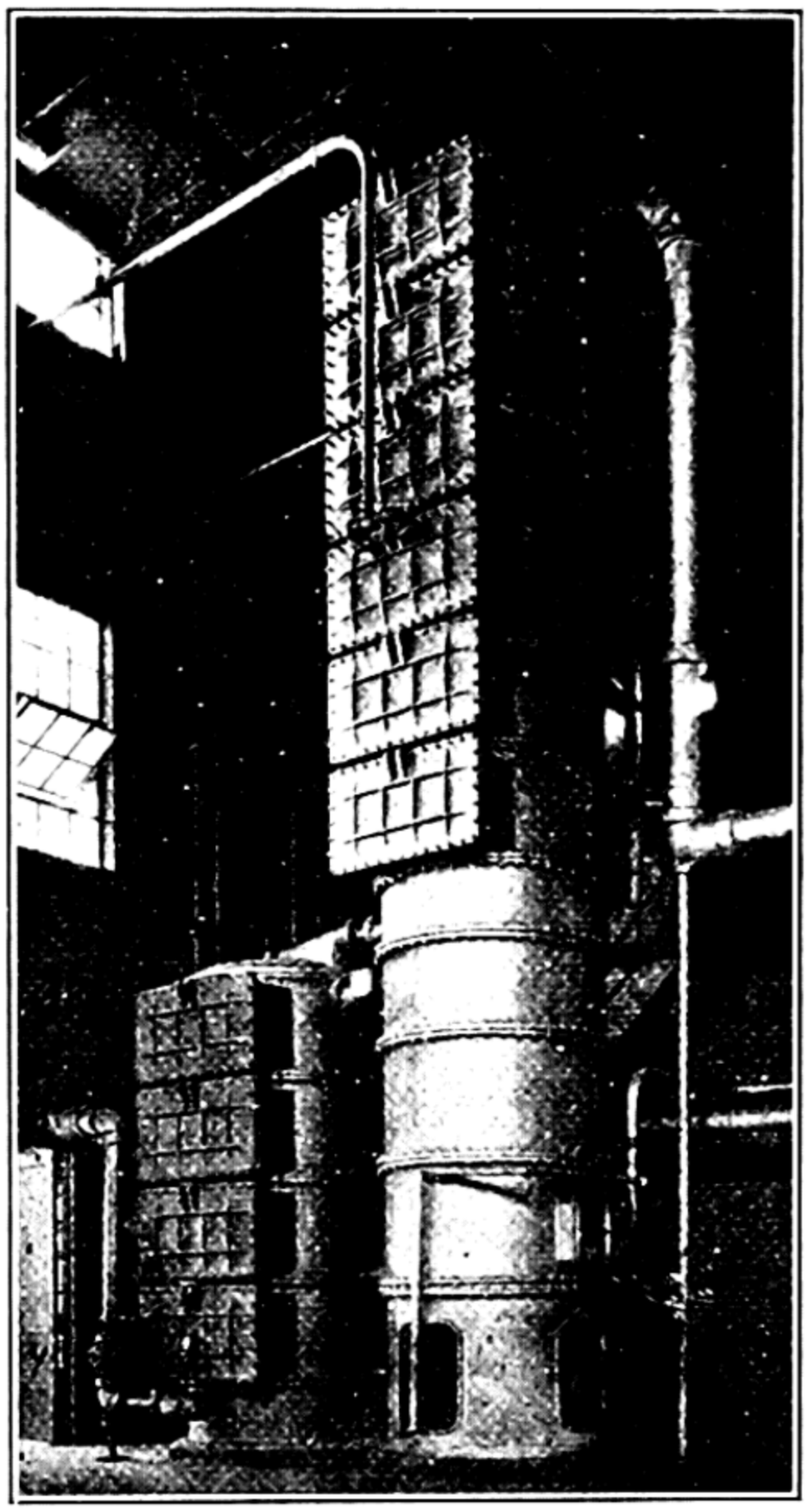


FIGURE 117.—Ammonia still with continuous operation. At the right, the lime leg surmounted by column for free ammonia distillation; at left, the fixed leg. *See* diagram in Figure 118. (Courtesy of the Koppers Construction Co., Pittsburgh, Pa.)

then carbazol, a solid; the latter is washed with solvent naphtha and sublimed; the product is 85 to 90 per cent carbazol.[24]

Other substances such as dicyclopentadiene are recovered from coal-tar fractions in smaller quantities. A table with all the carbon compounds isolated from coal tar will be found in a recent publication[25]; they number 116, without counting the homologs.

Benzene. The uses for benzene in chemical technology have increased steadily; on the other hand, the supply of benzene has been limited, for its production from coal by distillation is governed by the demand for coke and gas. The production of benzene is incidental to the production of the two specialized fuels, and unlike the production of toluene, no other good commercial source has been established. It is estimated that there will be

[24] The formulas of many of these compounds will be found in Chapters 27 and 28

[25] *Trans. Inst. Chem. Eng. (London)*, 22, 49 (1944).

available in coke-oven light oil 165 million gallons of benzene in 1949; an incomplete list of uses, namely for making phenol, styrene, nitrobenzene, aniline, and chlorobenzene, calls for 155 million gallons.[26] In addition, about 40 million gallons are required for making D.D.T., nylon, detergents, diphenyl, maleic anhydride, solvents, and miscellaneous substances. The hope is that some other source material may be substituted for benzene in

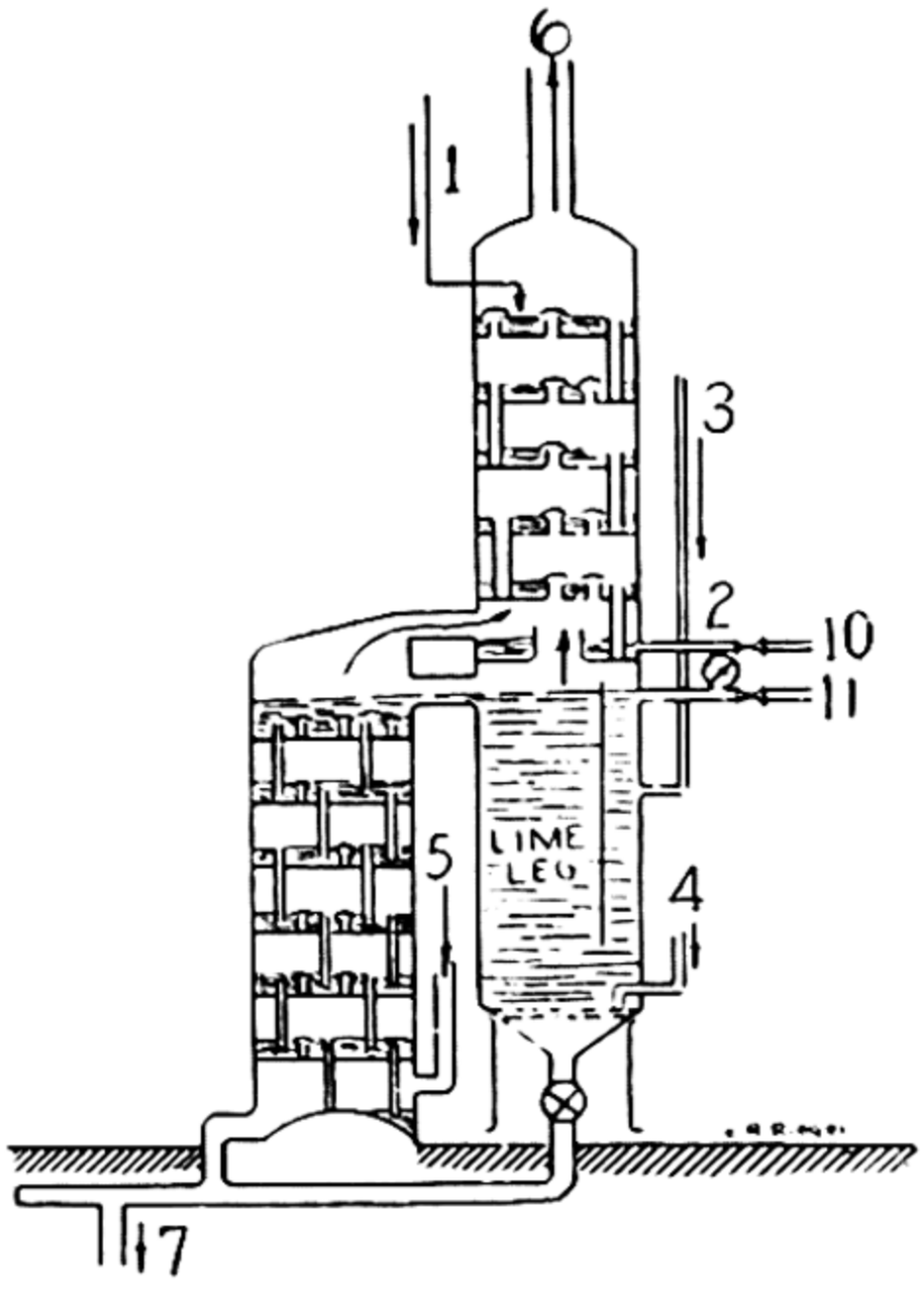


FIGURE 118.—Operation of ammonia still with continuous operation; Koppers system. 1, liquor inlet into the free still; 2, by-pass to the lime leg or mixing vessel, receiving lime at 3 and steam at 4; the milky suspension overflows to the fixed leg, receiving steam at 5; 6, ammonia vapors outlet; 7, waste pipe to sewer.

one or more of these processes, or that a new source of benzene, perhaps based on petroleum, may be found and developed. The synthesis of hydrocarbons in the new liquid fuel processes does not furnish benzene. Naphthalene is similarly in great demand, yet it is available only in limited supplies. The price of benzene is 3 cents a pound (formerly 2 cents), and that of naphthalene is 6 cents (formerly 3 cents).

Low-Temperature Carbonization. By carbonizing at a lower temperature than customary, a higher yield of liquid products, resembling oil rather than tar, may be obtained. The oven wall temperature in usual practice is 2350° F. (1288° C.); in the low-temperature processes, it would be 1300° F. (704° C.) and less. The difficulty is to perform the carbonization in reasonable time; the temperature is so low that the rate of its penetration is also low. Very thin layers of coal have been tried; also carbonization by passing in hot producer gas. For the present, the low-temperature processes are not of industrial importance in the United States.[27]

[26] Compare: "Benzene, supply and demand," F. W. Sullivan, *Chem. Eng. News*, 25, 2000 (July 14, 1947). "Economic trends in coal tar hydrocarbons," John M. Weiss, *Chem. Eng. News*, 26, 238 (January 26, 1948). "Supplies of benzene and naphthalene," an address delivered at Cleveland, Am. Inst. Chem. Eng. (May, 1948) by John M. Weiss.

[27] "Lessons from low temperature carbonization," R. P. Soule, *Proc. Intern. Conf. Bituminous Coal, 3rd Conf.*, Pittsburgh, Pa., 1, 272-298 (1931).

Ammonia Distillation. The ammonia still shown in Figures 117 and 118 liberates ammonia gas in two distinct steps. The upper part of the tall vessel, to the right in Figure 118, is a six-plate tower, each plate having caps and run-down pipes. The liquor to be distilled is fed in at the top plate; the free ammonia is driven out by heat alone. By free ammonia is meant ammonium hydroxide, sulfide and carbonate. At the last plate, a liquor collects which has no free ammonia, but still contains fixed ammonia, that is, sulfate or chloride, which must be treated with lime in order to liberate the ammonia gas. This liquor runs through by-pass 2 (*see* Figure 118) to the lower part of the taller vessel, where milk of lime is sent in. Liquor and lime mix thoroughly by the time they reach the overflow to the fixed leg, where they travel downward over plates with caps and through the run-

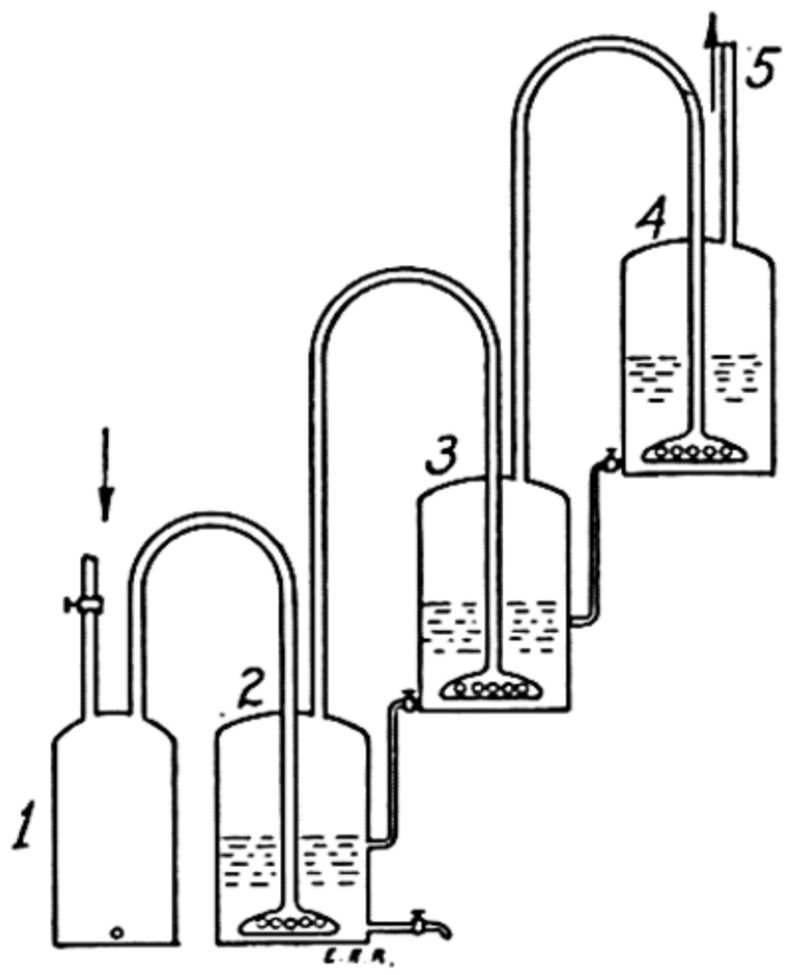


FIGURE 119.—Absorption of ammonia in water, using lead absorption bottles; the rich gas enters through trap 1, bubbles through 2, then 3, finally 4, and passes out, free from ammonia, at 5; the amount passing out is very small. The water from 4 is run into 3, and this into 2, where it is brought up to strength. Each bottle has a lead cooling coil, not shown.

down pipes to the waste pipe 7. A strong flow of steam enters near the base of the fixed leg, driving out the ammonia completely; the latter passes upward into the free still and with the ammonia from that still, passes through a dephlegmator to the saturators, where ammonium sulfate is produced.

The same still may be used to produce ammonia aqua. For this purpose it is necessary to retain hydrogen sulfide and carbon dioxide; this is done by an additional caustic soda wash, in a short column with plates and bubble caps. The purified ammonia gas is absorbed in lead bottles. (*See* Figure 119.)

In regular coke-oven practice, the ammonia still receives only a small part of the total ammonia in any form; the bulk of the ammonia in the coal passes directly to the saturators while still in the coke-oven gas, as stated under Ammonia Extraction. It is the increment in the ammonia liquor used as cooling spray which is sent to the still, together with the water layer from the condensate in secondary coolers.

A certain amount of gas liquor will always have to be distilled because small gas plants scrub their gas free from ammonia by water. The resulting liquor is usually concentrated by a preliminary distillation, and sold to a chemical firm, where it is made into aqua or ammonium sulfate. In

order to make sulfate, the still just described would be employed to furnish the ammonia gas, impure with hydrogen sulfide and carbonate, and this gas would be passed through a lead distributing pipe into a sulfuric acid solution partly saturated with ammonia. The salt formed may be shoveled out by hand or may be removed by a steam ejector. The unabsorbed gases are piped under a fireplace, so that only sulfur dioxide and carbon dioxide need be discharged into the atmosphere.

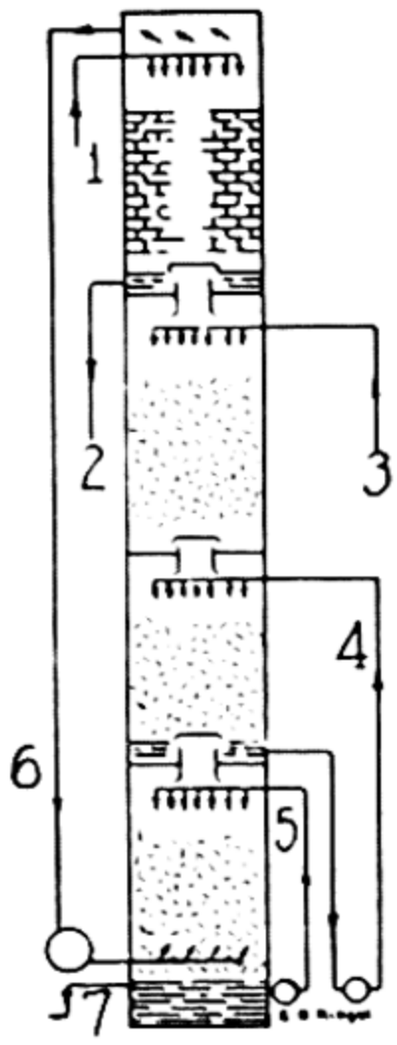


FIGURE 120.—Apparatus for dephenolizing ammonia liquors in coal distillation plants, by inert gas circulation (Koppers system). 1, phenol-bearing liquor; 2, phenol-free liquor; 3, fresh caustic solution; 4, circulated No. 2 caustic solution; 5, circulated No. 3 caustic solution; 6, inert gas laden with phenol vapors; 7, sodium phenolate solution outlet.

The reactions with lime are:

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O;$$
$$(NH_4)_2 + Ca(OH)_2 \rightarrow 2NH_3 + CaSO_4 + 2H_2O.$$

In the free still, they are:

$$(NH_4)_2S \rightarrow 2NH_3 + H_2S; \quad (NH_4)_2CO_3 \rightarrow CO_2 + H_2O,$$

and several others in small proportion.

De-phenolizing Ammonia Waste. The chlorination of city water has led at times to a bad taste, traced to a phenol content in the water, originating in the waste from the by-product ammonia still in a city gas plant or in any coke plant. The phenol is removed by taking the ammonia liquor at outlet 10 in the working sketch of the Koppers still (Figure 118), and sending it through a de-phenolizing system such as shown in Figure 120, wherein the phenol is removed in vapor form by an inert gas, which then is scrubbed by caustic. Sodium phenolate is formed, which is collected and removed to a storage tank; later the phenol is regenerated by treating with an acid. The phenol-free liquor returns by inlet 11 to the ammonia still, to receive the lime treatment.

Towers in which finely divided liquid benzene rises through the ammonia water, dissolving any contained phenol, are also in use; four unpacked towers are used, and the benzene travels counter-current to the ammonia liquor.

Other Patents

U. S. Patent 1,888,465, operation of by-product coke oven plant; 1,891,129, coke extractor for vertical (West) carbonization retorts; 1,841,036, enriched water gas and high-grade coke from caking bituminous coal; 1,838,294, coke oven battery (Becker); 1,805,922, horizontal coke oven (Otto); 1,829,608 and 1,787,490, vertical chamber coke oven; 1,787,963, coking retort oven; 1,832,181 and -2, coking retort oven; 1,832,612 and -3, coke oven (Becker); 1,893,145, on distilling tar residue by direct contact with hot gases at high temperature; 1,888,235-6, passing hot coke-oven gas through successive sprays of coal tar immediately after gas leaves the oven; 1,844,892, 1,862,494, 1,868,394-5, 1,871,550, on using by-product recovery system of coke-ovens to recover clean tar oils; 1,871,596, continuous distillation by bringing tar into indirect counter-current heat exchange relation with hot coke-oven gases; 2,416,476, briquetting of coal dust. Brit. Patent 569,918, recovery of ammonia in the coking industry. Xylene, toluene and benzene by cracking coal naphthas, U. S. Patent 2,395,161; pyridine recovery process, 2,393,666. Gasification of low-grade coals, Australian Patent 118,798.

Problems

1. A by-product coke plant disposes of 3200 gallons of motor spirits per day, which is also the daily production. Using the yield figures in the text, how much coal was distilled?

2. For the production of 315 tons of ammonium sulfate, how many tons of coal are coked, if the yield figures in the text apply?

3. In a Woodall-Duckham vertical retort, a coal is gasified which contains on analysis 19 per cent of combustible volatiles. Each ton of coal furnishes 13,350 cu. ft. of clean gas, ready for the holder. How much gas is due to the steam-on-coke reaction? (For water gas relations, *see* next chapter.) The gas from the coal proper occupies 20 cu. ft. per pound of weight.

Reading References

"Low-temperature carbonization," David Brownlie, *Ind. Eng. Chem.*, 19, 39 (1927), and preceding eight articles.

"Low temperature carbonization of coal," S. W. Parr, *Ind. Eng. Chem.*, 21, 164 (1929).

"The technology of low temperature carbonisation," Frank M. Gentry, Baltimore, Williams and Wilkins Co., 1928.

"Methods, apparatus used in determining the gas, coke, and by-product making properties of American coals," A. C. Fieldner, J. C. Davis, R. Thiessen, E. B. Kester and W. A. Selvig, *Bur. Mines. Bull.* No. 344, 1931. This bulletin contains 18 micrographs of thin sections of coal, showing microspores and macrospores.

"Improvement of design of coal-carbonizing equipment," Horace C. Porter, *Ind. Eng. Chem.*, 24, 1363 (1932).

"Present day knowledge of coal." Harry A. Curtis. *J. Soc. Chem. Ind.*, 51, 350 (1932).

"Coal tar distillation and working up the tar products," Arthur R. Warner, New York, D. Van Nostrand Co., and London, John Allan and Co., Ltd., 1914.

"The constituents of coal tar," P. E. Spielman, New York and London, Longmans, Green and Co., 1924.

"The higher coal tar hydrocarbons," A. E. Everest, London, and New York, Longmans, Green and Co., 1927.

"The distillation of coal tar," John M. Weiss, *J. Soc. Chem. Ind.*, 51, 219 (1932).

"A sulfate of ammonia plant," F. A. Ernst and W. L. Edwards, *Ind. Eng. Chem.*, 19, 768 (1927).

"Phenol recovery and treatment works of the Hamilton Coke and Iron Company," B. F. Hatch, *Ind. Eng. Chem.*, 21, 431 (1929).

"Elimination and recovery of phenol from coke plant ammonia liquors," R. M. Crawford, p. 966, and from crude ammonia liquors, p. 168, *Ind. Eng. Chem.*, 19, (1927).

"Phenols of low-temperature tar. Part I," Gilbert T. Morgan and Alfred E. J. Pettet, *J. Soc. Chem. Ind., Trans.*, **54**, 19 (1935).

"A text-book of American gas practice," Vol. I—Production of manufactured gas," Jerome J. Morgan, Maplewood, N. J., Jerome J. Morgan, 1931.

Glund's "International Handbook of the By-Product Coke Industry," American edition by D. L. Jacobson, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1932.

"Electrical removal of gum-forming constituents from manufactured gas," W. L. Shively and E. V. Harlow, *Trans. Electrochem. Soc.*, 69, 495 (1936).

"Underground gasification of coals" (Podzemgas), P. A. Chekin, A. I. Semenoff and J. S. Galinker, *Trans. Chem. Eng. Congress, World Power Conference, London* (1936), vol. III, paper E 12.

"The recovery of benzol by active carbon," H. Hollings and S. Hay, *J. Soc. Chem. Ind.*, 53, 143 (1934).

"Carbonization of typical bituminous coals-effect of rate of heating and final maximum temperature," Wm. B. Warren. *Ind. Eng. Chem.*, 30, 136 (1938).

"Research on coal tar. Part II.," E. A. Coulson and J. I. Jones, *Ind. Chem. (London)*, 22, 579 (1946).

"Coal and chemical industry," J. G. Bennett, *Trans. Inst. Chem. Eng. (London)*, 22, 43 (1944).

"Benzene-supply and demand," F. W. Sullivan, Jr., *Chem. Eng. News*, 25, 2000 (1947).

"Coal chemical industry, trends and problems," P. J. Wilson, Jr. and J. H. Wells, *Chem. Eng.*, 52, 110 (Dec. 1946).

"The history and present practices of the tar distillation industry," *J. Junior Inst. Engrs. (London)*, 55, 325-62 (1945).

"Use of Illinois Coal for the Production of Metallurgical Coke," F. W. Reed, H. W. Jackman, O. W. Rees, G. R. Yohe, and P. W. Henline, Illinois State Geol. Survey, Bull. No. 71, 132 pp. (1947).

"Modern Coke Ovens—the Basis of a Chemical Industry," E. V. O'Neill, *Iron Steel Eng.*, 23, No. 6, 96-8 (1946).

"Industrial Wastes, Coal and Gas Industry," H. A. Gollman, *Ind. Eng. Chem.*, 39, 596-601 (1947).

"Low Temperature Carbonization of Alaskan Coals," W. H. Ode and J. D. Davis, U. S. Bureau of Mines, Tech. Paper 668, 16 pp. (1944).

"Chemistry of Coal Utilization," T. A. Hendricks, John Wiley and Sons, Inc., New York.

"Chemistry of coal utilization," H. H. Lowry, New York, John Wiley and Sons, 1945.

"New bases from coal-tar," G. D. Bieber, *Chem. Industries*, 61, 51 (1947).

Fuel in the form of gas under slight pressure offers many advantages; its distribution costs little, once the pipes are laid; it is ashless, smokeless, and its application requires very simple devices. The use of combustible gas in municipalities is increasing, in spite of the newer electrical heating devices. In the industries, gas is largely employed as a fuel.

Chapter 15

Combustible and Illuminating Gas, Water Gas, Producer Gas and Natural Gas

The typical combustible gases which are manufactured are coal gas, coke-oven gas, water gas, producer gas, and oil gas; natural gas is obtained from the earth.

Coal gas and coke-oven gas are very similar; both are made by the distillation of bituminous coal. By coal gas is meant the gas made in the smaller retorts, either horizontal or vertical, in which coal is distilled primarily for the gas it yields; coke-oven gas is made in coke ovens, with coke and gas both primary products. Coal gas is high in illuminants (benzene, ethylene); in former years, it was still higher, for the original horizontal retorts had a vapor space over the coal which was exposed to the same high heat as the coal itself, and in this space nearly all the tar and oil was "cracked," producing mainly illuminants. Since the introduction of vertical retorts, filled over the whole cross-section with coal, less cracking takes place, and coal gas resembles more closely the gas from coke ovens, in which such cracking is also restricted.

Water gas is an entirely different product; it is made by the intermittent passage of steam into a bed of incandescent coke or other fuel. As the heat goes down, the injection of steam is interrupted, and a draft of air admitted until the coke reaches incandescence again. Except for unimportant impurities, water gas consists of hydrogen and carbon monoxide.

The manufacture of producer gas, on the other hand, is a continuous process; it is made by passing a mixture of steam and air into a bed of burning coke, anthracite, non-coking low-volatile coal, lignite, or peat. The resulting gas contains hydrogen and carbon monoxide as valuable constituents; as nearly half of it is nitrogen, its heating value is low. Producer gas is used, after careful cleaning, in gas engines (internal combustion). Mond gas is producer gas made at low temperature so that the ammonia in the coal may be conserved and later recovered. Blast-furnace gas [1] is also a form of producer gas.

Oil gas is made by "cracking" [2] suitable fractions of petroleum, in districts poor in coal and lignite, but rich in oil; it is rich in illuminants and has a high heating value.

Natural gas is obtained from the earth, chiefly by means of deep wells; the gas may issue from the well under pressure, or pumping may be required. It varies in composition, frequently containing a high percentage of

[1] Chapter 47.
[2] *Compare* the cracking of oil for gasoline, Chapter 24.

methane, and just as frequently, non-combustible impurities; in general, its heating value is very high.

There are many combinations of two or more of these typical combustible gases; the most frequent probably is that of oil gas and water gas, produced by enriching straight water gas by carburetted oil. In Buffalo at the present time the city gas consists of a mixture of coke-oven gas, water gas enriched by oil (hence containing oil gas) and natural gas.

The composition of several typical combustible gases is given in Table 48; the constitutents are listed in the order in which are are determined in the analysis; the figures are percentages by volume.

TABLE 48.—*Composition of typical combustible gases.*

	Straight coke-oven gas	Straight water gas	Water gas enriched by oil*	Producer gas	Naturalf gas
	Per cent				
Carbon dioxide (CO_2)	1.8	3.7	4.25	5.2	...
Benzene (C_6H_6)	.9	...	....	...	...
Ethylene (C_2H_4)	2.3	...	....	1.0	...
or other illuminants	...	...	10.33	...	...
Oxygen (O_2)	.8	.5	.71	.2	...
Carbon monoxide (CO)	5.5	42.3	31.60	26.3	...
Hydrogen (H_2)	49.2	47.9	35.38	14.4	...
Methane (CH_4)	30.3	.6	12.40	1.8	90.0
Ethane (C_2H_6)	...	...	....	...	8.8
Nitrogen (N_2)	9.2	3.4	5.33	51.1	1.2
Total combustibles	88.2	90.8	89.71	43.5	98.8
Btu. per cu. foot	555	299	574	155.6	1110

* 3.10 gallons of fuel oil per 1000 cubic feet of gas for enrichment.

† As to natural gas, other analyses will be found elsewhere in the book; it should be remembered that some natural gases contain sulfur, some contain nitrogen in sizable amounts, others helium, still others contain unsaturated hydrocarbons. For the analysis of a wood gas, *see* Chapter 16.

Inspection of this table will show that the heat values of coke-oven gas and straight water gas differ markedly, yet their percentage of combustibles is about the same. The reason is that the component compounds have different heats of combustion; hydrogen evolves 329 Btu. per cubic foot, measured at 62° F. and 1 atmosphere; carbon monoxide 322, methane 1003, ethane 1755. It is possible to compute the heat value of a mixed gas from the known values of the heats of combustion of the component gases; thus for the coke-oven gas listed in the table, the calculated heat value is 556 Btu.[3] while the observed value was 555. It may be noted also that producer gas has the lowest heat value; the same high temperatures which other gases furnish are nevertheless obtained with producer gas by preheating it in regenerators; the need of heating a vast volume of inert gases by the combustion itself is thus largely avoided.

The manufacture of coal gas and of coke-oven gas has been described in the preceding chapter.

[3] A part of this gas is distributed to townships near Buffalo, for direct consumption; it is therefore made slightly better than the New York State standard, 537 Btu.; there is no candle power standard in New York State. Another part of this gas is mixed with natural gas (one third), oil gas, water gas, and coke-oven gas; the final mixture has a minimum of 825 Btu. fixed by the State Commission, for delivery in the city of Buffalo and certain contiguous townships. The volume for the area served is 125 to 130 million cubic feet per day.

Water Gas [4]

Water gas is made by passing steam into a bed of incandescent coke; the temperature of such a fire is 1400° C. (2552° F.). Between the temperatures of 1400° and 1000° C. (1832° F.), the reaction

$$H_2O + C \rightarrow CO + H_2$$

takes place. As it proceeds, there is a fall in the temperature of the fire; the incoming steam must be heated. The reaction itself is endothermic, and heat is lost by radiation. With coke at a temperature below 1000° C., the steam reacts to form carbon dioxide, which is not desired, for carbon dioxide has no calorific value.

$$2H_2O + C \rightarrow CO_2 + 2H_2.$$

Hence the steam is stopped before the low temperature is reached, and the fire is brought back to its normal high temperature, 1400° C., by an air blast. Coke is consumed during the blast period, so that it could not be expected that all of it would be represented by carbon monoxide. Usually, between 50 and 60 per cent is transformed into the lower oxide; the rest burns to carbon dioxide, which escapes through a stack. There always are a few colder spots present, so that the second reaction takes place to some extent.

For many purposes, water gas is used as such; for sale in municipalities, it is usually enriched with oil gas, produced in a separate vessel forming part of the system. The gas-making period lasts 4 minutes; the air-blast or revivifying period, 2 minutes; the complete cycle is therefore 6 minutes. In order to use the hottest coke fully, the steam period is divided in two, and the steam sent in from below for one half, from above during the other half. Simultaneously with the change of direction of the steam, one of two gas valves open, so that the gas formed is led off in either case through a wide flue to the oil-gas vessel. After the steam has been on 3 minutes, the apparatus is purged for 1 minute, and then only is the air blast turned on. The operations and their duration are then: 1½ minutes for "up-steam," 1½ minutes for "down-steam," 1 minute for purge, and 2 minutes for air blast.

The complete generating apparatus consists of 3 vessels: the generator, the carburetor, and the superheater. All are steel vessels, cylindrical, of somewhat differing heights and diameters, as indicated in Figure 121; the generator is 10 feet in diameter and 15 feet high. The coke fire is in the generator; the coke charge is shoveled in through an opening in its top, level with the working floor. The steam for the up-blow enters below the fire through a perforated circular distributor; the gas made passes out through the upper valve in the 42-inch flue to the carburetor. For the down-blow, the steam enters above, and the gas passes out through the lower valve which lies in the same vertical plane as the upper; a flue leads the gas to the upper horizontal flue, so that this gas enters the carburetor in the same place as the up-blow gas. The valves are slot valves, and being exactly in one plane, are operated by one rod; the three-way steam cock

[4] Also called blue gas, because it burns with a blue flame.

is connected with levers to this rod, so that a single motion (small compressed air cylinder) makes all the changes simultaneously. The generator and flues are brick-lined.

The carburetor is filled with a checkerwork of bricks; during the air blast, the products of combustion stream through and raise its heat. During the steam period, the made gas, at high heat itself, enters near the top and passes downward, while an atomizer delivers oil at the top of the

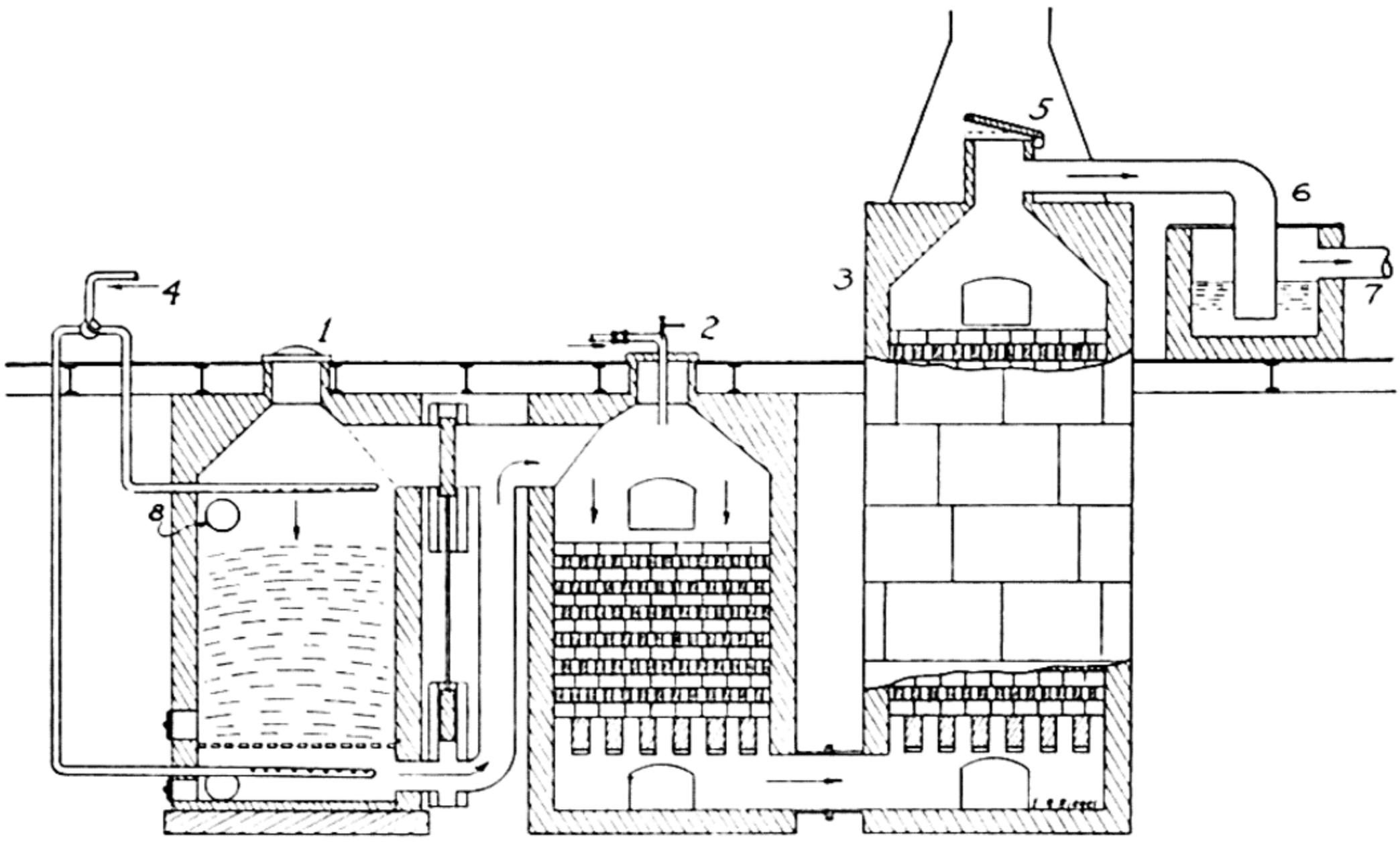


FIGURE 121.—Cross-section through a water-gas plant. 1, generator; 2, carburetor; 3, superheater; 4, steam inlet set for down-blow; the path of the gases is shown by arrows; valve 5 being closed, they pass through water box 6 to conduit 7 which leads to the purifying apparatus. 8 is the inlet for the blast during the revivifying period.

carburetor. The current of gas carries the mist of oil against the hot checkerwork; the greater part is reduced to molecular fragments which at normal temperature form gases; at the same time, a certain amount of tar is produced. From the base of the carburetor the gases pass to the superheater, in which they stream upward, to be delivered to the flue leading to the purifying apparatus. The superheater is also filled with bricks, and provides space and heat to carry out the oil-cracking and the thorough mixing of the gases. The path of the gases is indicated in the general illustration.

The three minutes of steam blow are followed by one minute of purge, during which steam enters at the top of the carburetor and sweeps out the good gas which remains in the carburetor and in the superheater. At the end of four minutes, the blast is turned on, to bring the fire back to incandescence; the products of combustion, after passing through generator and superheater, escape through a stack just above the latter, through a valve in the flue leading to the purifying apparatus. Each time the valve opens,

the waste gas catches fire with an explosion-like noise. Safety of operation is insured by interlocking devices, which permit the opening and closing of the several valves only in the proper order.

For a generator of the dimensions given, coke of the egg size is introduced in 820-pound lots; the production is about at the rate of 1000 cubic feet of straight water gas to each 40 pounds of coke consumed (total). To enrich this gas, varying amounts of fuel oil or special gas-oil fraction are used, for instance 3½ gallons per 1000 cubic feet of water gas; in the set described, this would require 20 gallons per cycle. The temperature in the carburetor lies between 1200 and 1300° F. (650° and 704° C.), and is measured by means of pyrometers.[5]

In an oil-gas plant, a generator and superheater are used, and the heat is furnished by an oil burner; otherwise the operation is similar to the one just described.

The coke consumed in manufacturing water gas, in 1945, amounted to 168,859 tons, valued at $8.45 a ton.

The Purification of Carburetted Water Gas. The flue leading away from the superheater dips in the water of the wash-box, where the small amount of tar is deposited; the gas then passes to the cooler, a nest of pipes laid in running water. From here it is pulled by exhausters and pushed into the purifying boxes containing the same lime-iron oxide-coated shavings which are used for coke-oven gas.[6] From the purifying boxes, the gas passes to the holders, ready for delivery. Metering and testing are performed by the continuous, recording Thomas meter or other meter and Thomas calorimeter already described (Chapter 14).

A water-gas plant is compact; it may be started at short notice, and when shut down for a given period is readily maintained in good condition. When part of a system supplying municipalities, it is usually shut down in the summer months, when the demand is light enough to be supplied by coke-oven gas or coal gas; it is placed in operation in the winter months.

Producer Gas

The modern producer is a steel vessel of moderate size, for example, 10 feet in diameter and 12 feet in height, brick-lined; in it any low-grade fuel may be partly burned, while steam in addition to air is sent into the fire. The operation is continuous; the fuel (for instance, low-grade coal) is dropped into the producer at a constant rate. A mixture of air and steam is served all the time. The resulting gas passes out continuously, and the ashes are removed constantly by a sweeper in the water seal at the base Such a producer is shown in Figure 122; it carries a water-cooled, rotating arm which levels the charge and prevents the formation of holes. The shell is stationary. The reactions are essentially the same as those which take place in a water-gas plant; but in producer gas there is contained all the nitrogen entering with the air for combustion; hence its total combustible constituents are low, and its heat value per unit volume also. Numerous forms of producers are on the market; in some of these, the shell rotates

[5] Chapter 46.
[6] For "liquid purification" see previous chapter.

The capacity of a producer 10 feet in diameter and 12 feet high with automatic operation is 3000 to 4000 pounds of coal per hour. The air-steam mixture is forced in by means of the steam which is applied to an air injector (see Figure 122); the composition of this mixture is approximately 7 volumes air and 1 of steam. The amount of steam used per pound of coal gasified lies between 0.3 and 0.5 pound, sometimes a little less (0.25); the amount depends upon the clinkering properties of the coal

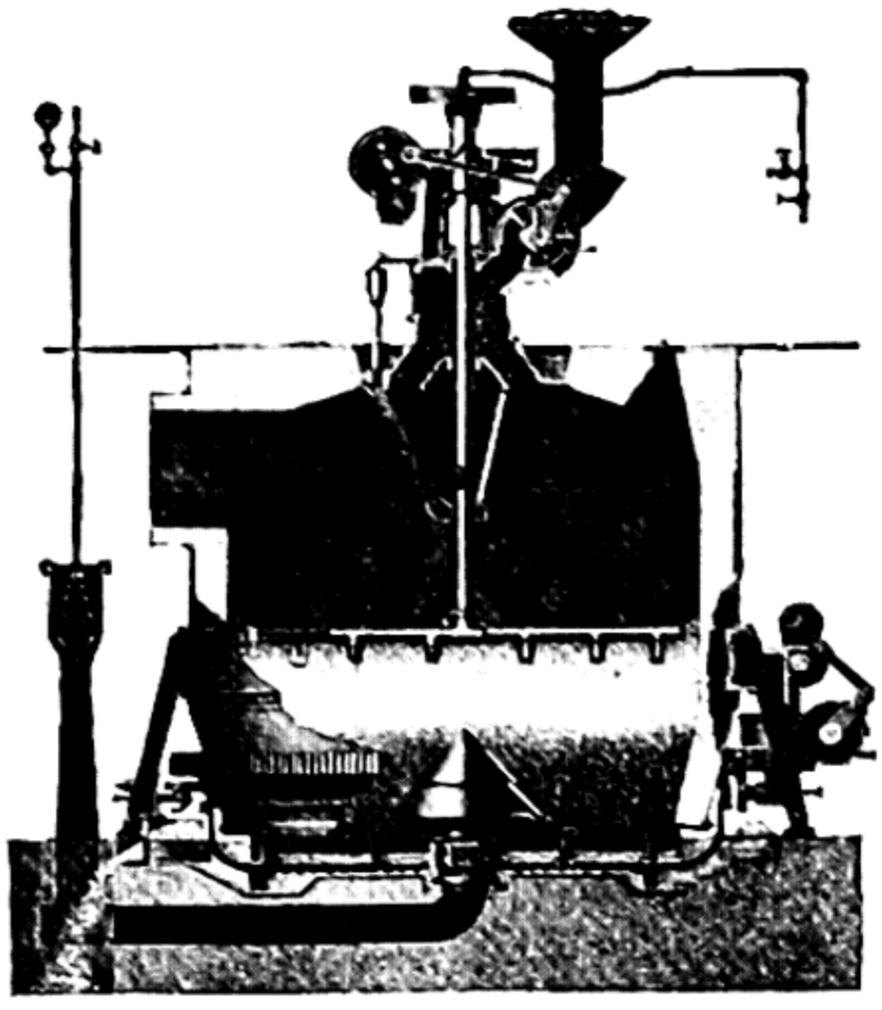


FIGURE 122.—The Chapman Gas Producer with stationary shell. (Courtesy of the Cooper-Bessemer Corporation, Mt. Vernon, Ohio.)

used. The volume of gas varies with the grade of coal. The following figures will serve as guides: 1 pound of bituminous coal yields 60 cubic feet; semi-bituminous, 30 cubic feet, and lignite, 28 cubic feet.

NATURAL GAS

Natural gas is found in regions which also have coal or oil, although the wells may be many miles away. Many gas wells do not yield oil, but an oil well almost always produces gas and oil; the gas is then known as casinghead gas. The gas from wells which yield no oil is usually rich in methane and contains some ethane and higher hydrocarbons; its composition remains fairly steady over long periods. The gas obtained with oil (petroleum) is at first methane essentially, but gradually becomes richer in the higher hydrocarbons, and poorer in methane; such gas when "wet" furnishes a very volatile gasoline, casinghead gasoline, which is largely used to mix with "cracked gasoline" deficient in low-boiling constituents. The methods for extracting gasoline from such gas are compression and cooling methods and absorption by a higher-boiling oil fraction, by charcoal, silica gel, or other absorbent. Gasoline extracted from natural gas in 1945 made a new record, 4,673,507 gallons which brought 4.56 cents per gallon. The production of gasoline from wet natural gas, for the leading states, expressed in millions of gallons, was as follows: Texas 1,045, California 653, Oklahoma 272, Louisiana 222, New Mexico 87, Kansas 59, Illinois 55, West Virginia 52, Arkansas 50, Wyoming 33, and Pennsylvania 13.

The gas remaining after gasoline removal is used as fuel, as is gas from wells [7] yielding no gasoline; but appreciable amounts are burned with an insufficient amount of air for the production of carbon black, or decomposed by heat to form carbon and hydrogen. The development of natural gas trunk pipe lines has brought about a distribution of this gas which makes it a rival of manufactured gas; as stated before, it is often admixed with coke-oven gas for domestic use. There is a gas trunk line from Amarillo, Texas, to Chicago; another to Indianapolis; in the south and southeast, a line runs from Shreveport, Louisiana, to Atlanta, Georgia. Trunk lines bring gas from the Hugoton-Panhandle field to Detroit, Minneapolis, Kansas City and Chicago, and from the Louisiana-Texas Gulf fields to St. Louis. A 26-inch and a 30-inch line bring gas from the Texas Panhandle to southern California; the capacity is or soon will be 305 million cubic feet of gas daily.[8] The "Big Inch" pipe line, 24 inches in diameter (1,254 miles of main lines) and the "Little Inch," 20 inches in diameter (1,475 miles), were originally oil lines; now they are used as gas lines, bringing southwestern gas to markets located in an area extending from Indiana to New England; their combined capacity is 508 million cubic feet of gas daily. The gas pipe lines will total, with the construction now in progress, approximately 247,000 miles by January 1st, 1949.

Natural gas serves mainly as a fuel; about 10 per cent of the yearly production is consumed in the manufacture of carbon black. A constantly increasing amount is used as a raw material for chemicals; in certain processes, natural gas plays the part of a chemical directly (*e.g.*, reduction in manufacturing magnesium). The utilization of natural gas for chemical products has been explored exhaustively and the results published.[9] Overshadowing all others is the manufacture of synthesis gas for the production of liquid fuels (Chapter 24).

The estimated proved recoverable reserves of natural gas in continental United States, as of December 31, 1946, are 116,440,336,000,000 cubic feet.[10]

The marketed production of natural gas for 1946 (U. S.) was 4,095 billion cubic feet, a new high record; the gross production would be about a third more. Roughly, half the gas is from oil wells, half from gas wells. Of the natural gas consumed, 94 per cent was treated for the removal of gasoline. The production for the leading states, expressed in billions of cubic feet, was as follows: Texas 1,711, Louisiana 543, California 502, Oklahoma 357, West Virginia 160, Kansas 146, New Mexico 105, Kentucky 82, Pennsylvania 82, Ohio 50, Arkansas 46, Wyoming 35, Montana 32, Michigan 22, Illinois 17, New York 9 (1945). The gross production is larger: in 1945, it was 5,902 billion cubic feet for the whole country. The difference is accounted for by gas used in repressuring, by losses and waste.

[7] The gas for the chemical laboratory of the University of Buffalo, within the city limits, is furnished by a gas well just outside the building; it is 900 feet deep; the pressure at the well is 200 pounds per square inch. The well has furnished gas under the same pressure for many years past. The amount of gas drawn is moderate.

[8] "Minerals Yearbook."

[9] "Utilization of natural gas for chemical products," Harold M. Smith and W. C. Holliman, I. C. 7347, Bureau of Mines (March, 1947).

[10] "Minerals Yearbook," 1946.

The average value of natural gas at the wells and unprocessed was 5.1 cents per 1,000 cubic feet in 1946; the residual gas, after washing out the gasoline, brought 1½ to 2 cents per 1,000 cubic feet in 1940. The total number of producing wells in 1945 was 60,660, and to these were added 3,090 wells drilled in 1946.

Not only in gas form, but also in the liquefied state is there a large movement of low molecular weight hydrocarbons, of petroleum as well as of natural gas origin. In 1946, the sales of such products were as follows: liquefied butane 438,439,000 gallons; liquefied propane 548,827,000 gallons; liquefied butane-propane mixtures 718,016,000 gallons. The liquefied hydrocarbons are shipped in tank cars and tank wagons, in cylinders and drums, and by pipe line. Domestic use (household consumption) accounted for 44.9 per cent of the sales of liquefied petroleum gases in 1946, gas manufacturing 5.1, industrial fuel, 9.3, synthetic rubber components 17.0, chemical manufacturing 18.1, and internal-combustion-engine fuel 5.6.[11]

The problem of meeting the peak demand for natural gas in the winter months has become more acute as the practice of heating dwellings by gas has spread. In the cities, the gas distributed through the mains is generally a mixture of coke-oven, coal and natural gas, sometimes with added water gas, more rarely oil gas. Natural gas has been relied on more and more to make up any deficiency in supply. The natural gas companies have met the demand, at least in part, by increasing pipe lines, by increasing the volume of gas delivered by a given line, and by means of underground storage. Gas obtained from wells during periods of low demand may be pumped into exhausted gas sands, to be withdrawn again in the winter months, when the demand is high. The storage wells are selected for their location convenient to the market, and for their geological structure, which must be such that no loss of gas occurs. One company operating in Ohio and West Virginia had a total of 38.5 billion cubic feet of gas stored in 17 underground storage pools at the close of 1947. The approximate equivalence of gas stored and gas withdrawn is indicated in Figure 123. An Illinois utility company has made a new departure in underground storage of natural gas; a number of parallel sections of large diameter pipe are installed a few feet underground and filled with gas at a pressure of 2,250 lbs./sq. in.[11] Not only natural gas, but coal gas and water gas are now stored underground and successfully withdrawn, without appreciable loss.[12]

Storage of liquefied natural gas in insulated spherical nickel-steel containers in East Cleveland[13] so that the early afternoon and early morning peak demands might be accommodated without the construction of additional gas lines, came to an end when a disastrous fire wrecked two of the spheres (October, 1944). There are no plans for rebuilding.

[11] "Minerals Yearbook," 1946.

[12] "Storage of coke-oven gas in sandstone strata," J. Russell Bircher, *Chem. Eng. Progress*, 43, 453 (1947).

[13] "Liquefying natural gas for peak load supply," by R. W. Miller and J. A. Clark, *Chem. Met. Eng.*, 48, January, p. 74 (1941).

A different method [13a] which deserves attention consists in catalytically cracking a mixture of propane vapor (or butane, or propane-butane), air, and steam over refractory cubes impregnated with nickel oxide, held in vertical, chrome-nickel alloy cracking tubes. The latter are heated by oil burners. The reformed gas with 26.2 per cent CO, 45.5 per cent H_2, 26.2 per cent N_2, 1.1 per cent CO_2, and 1 per cent CH_4 issues from the tubes in a continuous stream. Its heating value is 237 Btu/cu. ft. It is cooled, then

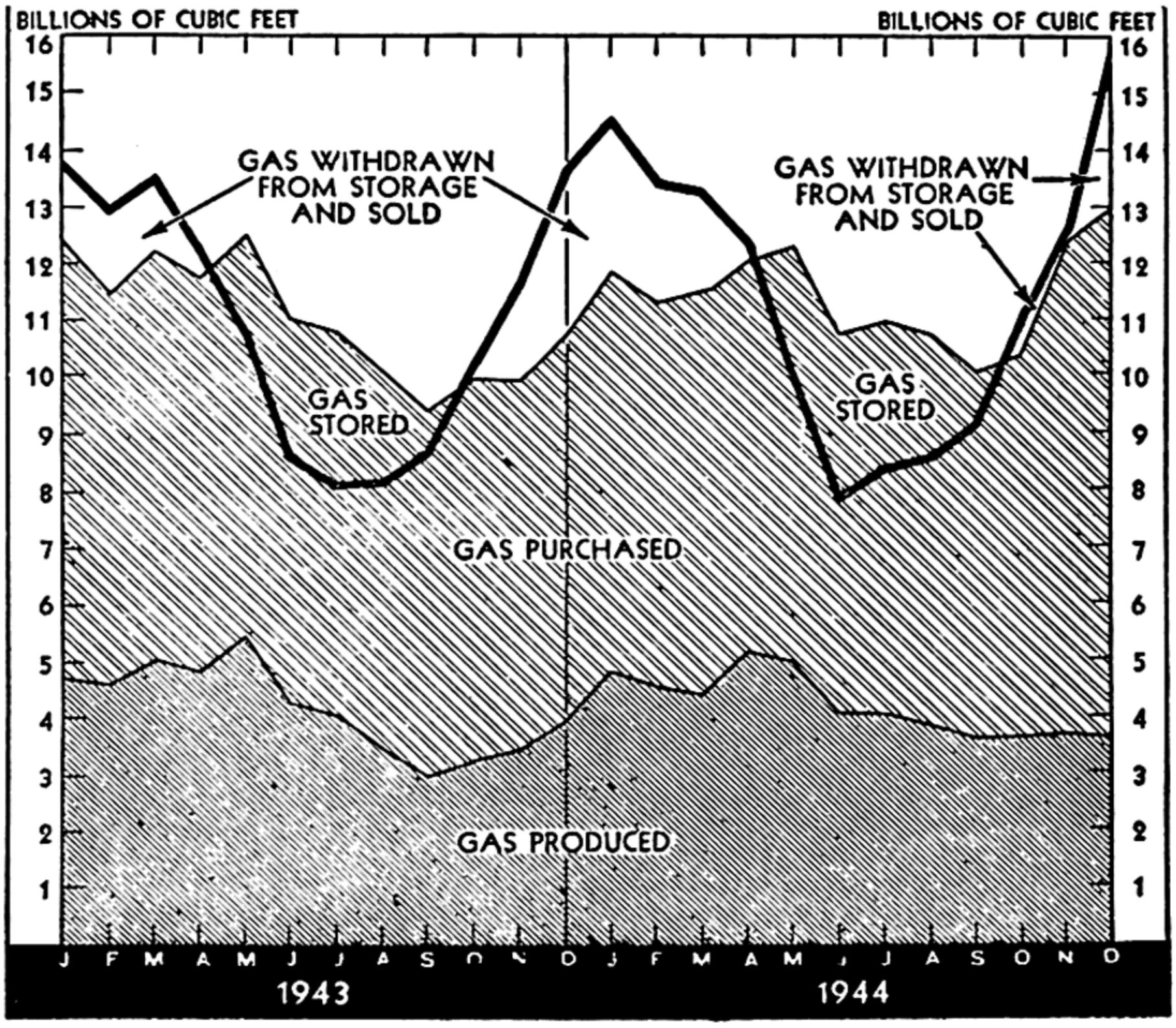


FIGURE 123.—A visualization of the amount of natural gas stored underground, and withdrawn, with essentially no loss. (Consolidated Natural Gas Co., N. Y., Annual Report to stockholders.)

enriched with the same propane in vapor form to produce a final gas with 540 Btu/cu. ft., containing 14.3 per cent C_3H_8. The striking attribute of this process is that it produces a complete substitute gas. With ordinary gas, 22 per cent enrichment of the base gas is the limit.

Pintsch gas is a compressed oil gas. Blau gas is a mixture of propane, butane, pentane, and hexane containing hydrogen and methane in solution under pressure. The solution is handled in strong steel cylinders. Acetylene is presented in Chapter 19. For isolated laboratories a satisfactory burning gas is obtainable by bubbling air through a low-boiling gasoline; the operation is automatic, a reduction in pressure of the gas causing a water valve to open, whose flow rotates a water turbine which carries the fan.

[13a] "The catalytic cracking process as a means of peak load shaving," S. W. Horsfield, American Gas Association, 1948 meeting at Asbury Park, N. J. The process is in operation at Riverhead, Long Island, N. Y.

Another convenient gas for isolated laboratories is "Pyrofax," which is propane, C_3H_8 (boiling point $-42.5°$ C.) compressed in steel cylinders which are transportable. Similar "bottled gases" are "Philgas," "Essotane," and many others.

Surface Combustion

Surface combustion is flameless combustion; it takes place when gas with the theoretical amount of air strikes lumps of refractory materials which are at high heat; this material glows, and high temperatures are obtained. Instead of lumps, a slab or a brick wall may be used. The advantages of this method of combustion are that the combustion is accelerated, that the energy appears largely as radiant energy which is rapidly transmitted, and that the source of this energy is concentrated. Furnaces have been heated by this method, but of special interest is the operation of a boiler[14] with fire tubes which were filled with refractory fragments on which the combustion took place. The boiler was 4 feet long, 10 feet in diameter, and without brick setting; the generation of heat took place within the 4-foot fire tubes. This unusual method of heating promises important economies.

Surface combustion is a catalytic process; the combination of gas and oxygen is accelerated by the contact substance, here fragments of firebricks. It may be applied with water gas, coke-oven gas, natural gas; whether producer gas may be used is not quite settled.

Other Patents

U. S. Patent 1,880,010, continuous generation of water gas by use of pulverized fuel and steam; 1,855,309, water-gas generator and process for making combustible gas; 1,833,964, process for making water-gas of a high Btu.; 1,829,767, 1,828,461, 1,788,400, and 1,827,169, processes for making carburetted water gas; 1,814,580, process for making producer gas; 2,029,317, gas making apparatus, process for catalytic conversion of hydrocarbon fluids into fuel gas by reacting a hydrocarbon with steam in the presence of a catalyst at high temperature.

Problems

1. The composition of the several commercial combustible gases in the text are volume percentages. The heat of combustion for the several constituents in pure form is as follows: Ethylene, 1591 Btu. per cubic foot; carbon monoxide, 322; hydrogen, 329; methane, 1003; ethane, 1755; benzene, 4004 (for low percentages only); disregard the non-combustible gases. Compute on the basis of the percentage composition and the heat value for the substance, the heat value or heat of combustion for the several mixed gases given in the table; compare with the Btu. value reported there. There should be close agreement. These figures are all in terms of the "high Btu." results. (Figures from Marks' "Engineering Handbook," New York, McGraw-Hill Book Co.)

2. Find the corresponding volumes of typical combustible gases which must be burned to fit Problem 1, Chapter 12, in cubic feet at 62° F. and atmospheric pressure.

3. It is necessary to furnish 50,000 cu. ft. of producer gas per hour to a furnace. Using the yield figures given in the text, how many pounds of bituminous coal, semi-bituminous, and lignite will be required per day?

[14] "Coal and its scientific uses," William A. Bone, who developed this boiler. London and New York, Longmans, Green and Co., p. 445, 1918, or *Proc. Am. Gas Institute*, 6, 565 (1911).

Reading References

"Coal carbonization," Horace C. Porter, New York, Chemical Catalog Co., Inc., 1924.

"The recovery of gasoline from natural gas," George A. Burrell, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1925.

"Manufacturing plant of the Providence Gas Company," *Chem. Met. Eng.*, 21, 34, 88 (1919).

"Modern gasworks practice," Alwynne Meade, Ernest Benn, Ltd., London, 1921.

"Natural gas handbook," J. C. Diehl, American Meter Co., Erie, Pa., 1927.

"Handbook of casinghead gas," H. P. Westcott, American Meter Co., Erie Pa.

"Long distance transportation of natural gas," Edgar G. Hill and George I. Rhodes, *Trans. Am. Inst. Chem. Eng.*, 25, 58 (1930).

"New processes aid in manufacturing clean gas," D. L. Jacobson, *Chem. Met. Eng.*, 36, 58 (1929), includes a description of a waterless gas holder.

A map showing the natural gas trunk pipe lines in the United States may be obtained at a nominal price from the Oil and Gas Journal, Tulsa, Okla.

"Natural gas, its production and distribution," G. R. Hopkins, *Ind. Eng. Chem.*, 22, 502 (1930), with a map of the principal natural gas lines.

"Industrial gases," H. C. Greenwood, London, Balliere, Tyndall, and Cox, 1920.

"Gas calorimetry," C. G. Hyde, London, Ernest Benn, Ltd., 1932.

"The hydrogenation-cracking of creosote for motor fuel," C. M. Cawley, C. C. Hall, J. G. King, *J. Soc. Chem. Ind.*, 54, 58T (1935).

"A thermal study of the process of manufacture of water gas," A. Parker, *J. Soc. Chem. Ind.*, 46, 72T (1927).

"Liquefaction, storage and regasification of natural gas," J. A. Clark and R. W. Miller, *Gas Age*, 86, No. 9. October 24 (1940); see also *Gas Age*, 87, April 10, p. 25 (1941).

"First commercial liquefaction plant in full-scale operation," P. A. Condit and W. T. Burgess, *The Oil and Gas Journal*, 39, part 5. March 20, p. 46 (1941).

"Synthetic ammonia produced from natural gas," James A. Lee, *Chem. Met. Eng.*, 52, 94 (1945).

The store of coal in the earth was formed many thousands of years ago; when it is exhausted, man will not be able to replace it. It is different with wood, which can be grown in a few years. The scientific exploitation of the forest resources provides for replanting so that new wood grows at about the same rate as older wood is cut. To put the difference in another way: using coal means the exhaustion of capital; using wood means drawing on earnings only.

Chapter 16*

The Chemical Utilization of Wood: Extraction, Hydrolysis, Distillation

The three types of chemical utilization of wood described in this chapter are arranged in the order of increasing chemical change produced. Extraction removes only those constituents of the wood which are soluble in water or organic solvents, or which can be easily evaporated by means of steam. Hydrolysis renders the carbohydrate portion of the wood soluble in water, by the action of acids; there is left behind an insoluble lignin. Distillation causes a multitude of splitting and condensing reactions by subjecting the wood to high temperatures.

There are other chemical and semi-chemical utilizations of wood. The most important one is its conversion into cellulose pulp for making paper and other products (see Chapter 21). The compounding of sawdust and shavings with resins with subsequent compression into boards and panels is increasing in importance. Large amounts of wood flour, estimated at 65,000 tons a year in the United States, are used as "fillers" in compositions for plastic molding with phenol-formaldehyde and urea-formaldehyde resins. Still in the laboratory stage are methods of chemically splitting the wood substance in the presence of hydrogen, at high temperatures and pressures. Among the products of this hydrogenolysis are alcohols, ketones, phenols. and neutral oils.

Extraction

Turpentine and Rosin. Turpentine and rosin are obtained from the tapped sap of living coniferous trees, chiefly pines, or from the extracts from stumps left in the ground at earlier cuttings. The turpentine from slash pine is levorotatory, while that from longleaf pine is dextrorotatory.

Pure gum turpentine is obtained by steam-distilling the collected sap; it consists principally of terpene hydrocarbons of the general empirical formula $C_{10}H_{16}$. Wood turpentine is produced from stumps and top wood by destructive distillation ["DD"], or steam distillation ["SD"], by extraction with solvents ["SD"], or as by-product of the sulfate paper mills. The states most prominent in these industries are Florida, Georgia, Alabama, and Louisiana. The Scandinavian peninsula produces turpentine from the Norway pine; another producing area is along the coast in southwestern France.

*In collaboration with Dr. Eduard Farber, Chief Chemist, Timber Engineering Company, and Consulting Chemist, 4530 Brandywine Street, N.W., Washington, D. C.

For gum turpentine, the bark of the tree is cut, and the resin ducts are opened by incisions, leading into a cup which can hold one half to 1 gallon of sap. The application of sulfuric acid of 40 to 60 per cent concentration increases the rate and duration of the flow. The fluid is not the nutritive sap of the tree like that collected from the sugar maple. The sap flows from March to September. The collected sap is distilled from a copper still; turpentine and water pass over, and the rosin is left in the still. In some plants, steam is passed in from the beginning; in others it is introduced after

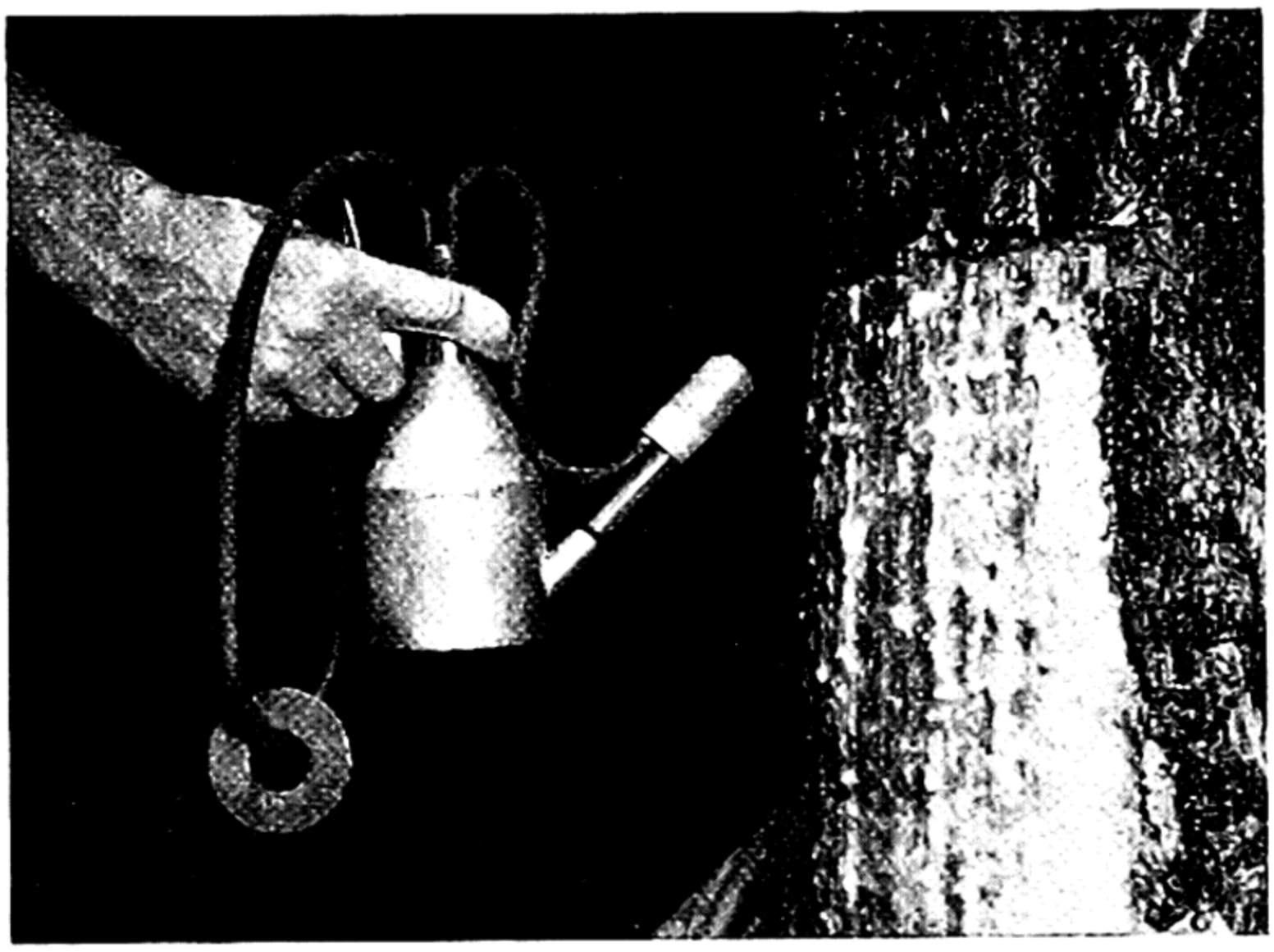


FIGURE 124.—Spraying a cut face on slash pine to stimulate the flow of gum.

the turpentine and water distillate stops, giving an additional amount. The average composition of crude gum is rosin 68 per cent; turpentine 20 per cent; water 12 per cent. The uses of turpentine are based mainly on its solvent properties in paints; its high content of pinene permits the manufacture of pinene hydrochloride, a solid, and other chemical substances.

For the crop year April, 1946, to March, 1947, there were produced in the United States: gum turpentine 270,286 barrels; SD wood turpentine 167,659 bbls.; DD wood turpentine 4,549 bbls.; sulfate wood turpentine 127,491 bbls. (1barrel=50 gallons). Total turpentine production was 569,985 barrels.

Gum rosin has been mentioned; it is run in the melted state from the bottom of the gum turpentine still into drums, where it solidifies. Wood rosin is the rosin extracted by solvents from the wood residue after steam distillation of stumps and "lightwood." In the same 1946/47 crop year, there were produced: gum rosin 744,086 drums; reclaimed gum rosin 8,449 drums; wood rosin 967,713 drums; total 1,720,248 drums (1 drum=520 pounds net). Some of the uses of rosin are given in Chapters 31 and 35. Other uses depend upon the nature of rosin: a mixture of unsaturated acids, mainly abietic acid and, depending upon the source, pimaric acid. Its sodium soap serves

in sizing material for paper, and in making the emulsion for manufacturing GR-S rubber.

Sulfate wood turpentine is the condensate, other than water, of the vapors periodically emitted from the top of the digesters charged with pine wood chips.[1]

The alkaline black liquor obtained in pulping resinous wood contains sodium salts which are separated as a soap. On decomposition with acids "tall oil" is produced from this soap as a brown oil with the following

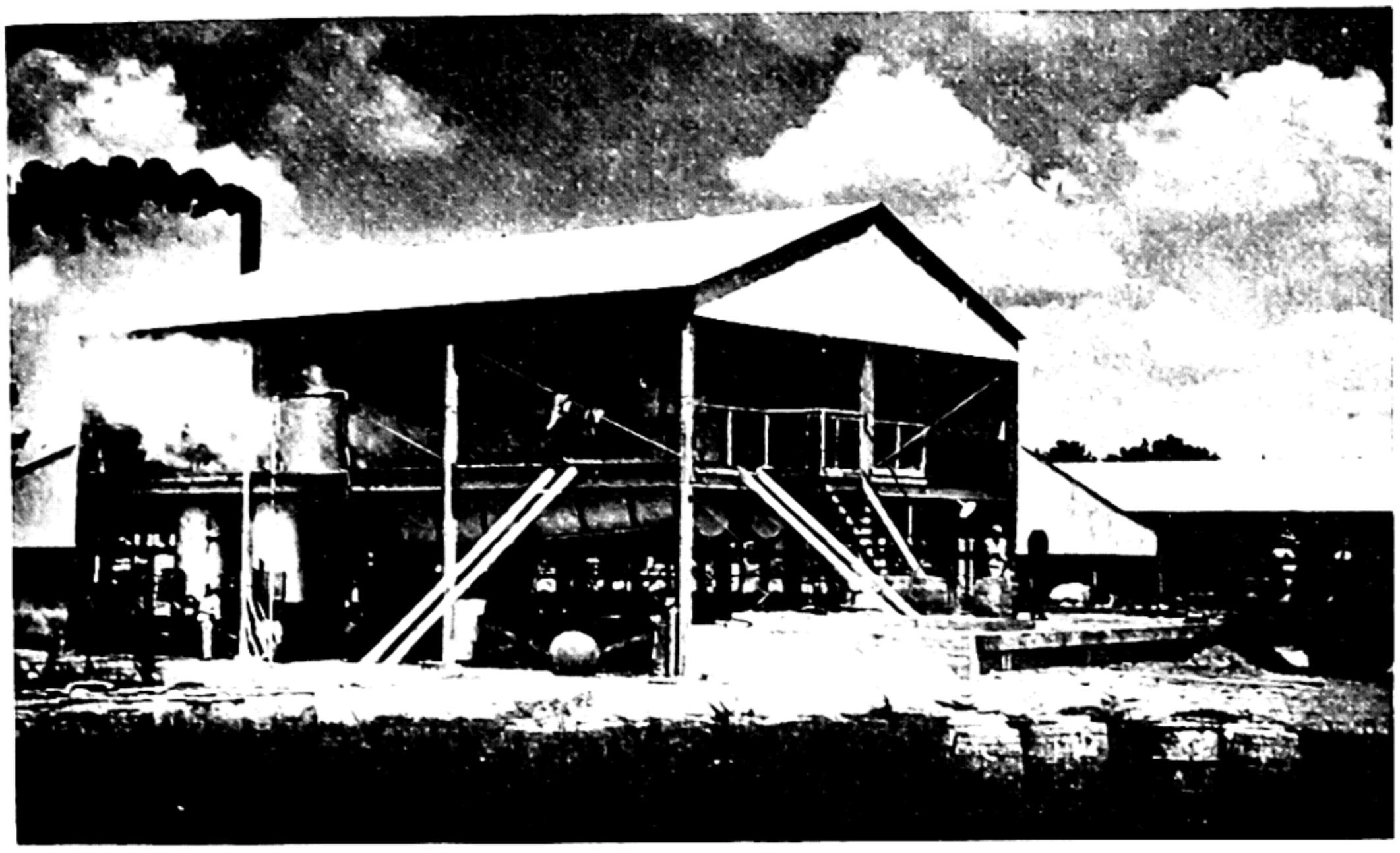


FIGURE 125.—View of a crude gum distilling plant.

average composition: 45 to 55 per cent fatty acids, 40 to 45 per cent resin acids, 6 to 10 per cent unsaponifiables. The production of crude tall oil in the 1946/47 crop year was 112,568 tons. It is one of the lowest-priced fatty acid materials. It is used for soaps, for emulsifiers, and to some extent as a plasticizer for synthetic rubber.

Pine oil is produced, together with turpentine, pine tar, dipentene and other monocyclic hydrocarbons, from the oil distillate of the wood. In the crop year 1946/47, the amounts were: pine oil 130,984 bbls., pine tar, 100,998 bbls., rosin oil 18,094 bbls., dipentene 27,320 bbls., "other monocyclic hydrocarbons" 40,120 bbls. (1 barrel = 50 gallons).[2]

During the war years, the price of turpentine was 80 to 90 cents a gallon, and rose to $1.33 in November, 1946. Early in 1948, it was around 70 cents a gallon. Rosin is about $6.85 per 100 lbs. for the dark grades, up to $8.50 for light grades of wood rosin, and $9.45 for gum rosin.

[1] "Turpentine recovery in pulp mills," *Pulp and Paper Magazine of Canada*, 48, No. 7, 79 (1947).

[2] All figures from Naval Stores Report of May 9th, 1947.

and two industrial methods have been studied and proved in large-scale plants: the Bergius-Rheinau method, based on the use of concentrated hydrochloric acid at ordinary temperatures, and the Scholler-Tornesch method, in which very dilute sulfuric acid is used at temperatures of 170 to 180° C. (338 to 356° F.). The latter method in an improved form is known in the United States as the Madison process, thanks to work done at the Forest Products Laboratory in Madison, Wis. A manufacturing plant embodying this process has been erected in the Willamette Valley in Oregon. It was leased by the owner, the Government, to a private company, and successfully operated for some time.

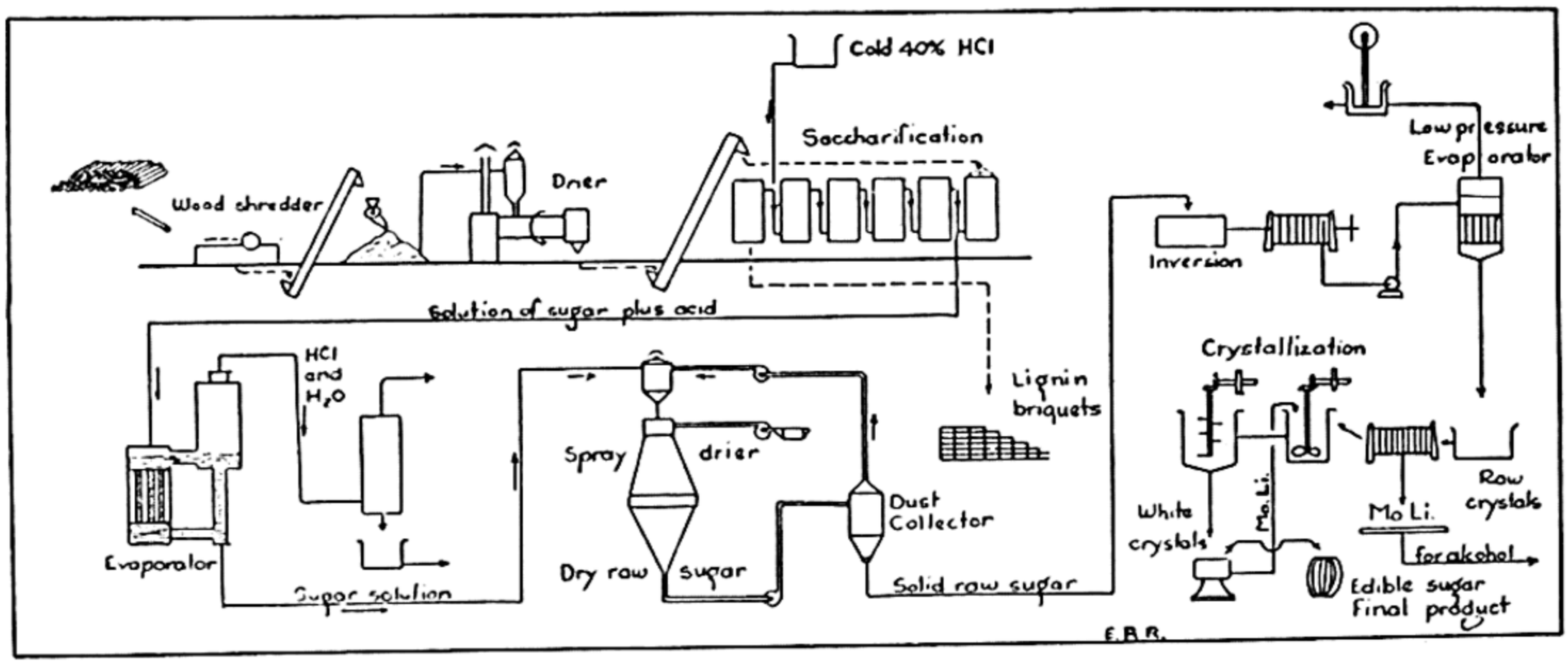


FIGURE 128.—Diagrammatic flow sheet for the Bergius wood hydrolysis process.

Bergius-Rheinau Process. Hydrochloric acid of about 40 per cent (by weight) is produced by reinforcing recovered, weaker acid with hydrogen chloride from salt-sulfuric acid retorts, or by burning chlorine with illuminating gas.

The strong acid enters that part of a battery of diffusers which contains the most nearly exhausted wood and is pumped through the next following containers until it is nearly saturated with the carbohydrates dissolved from the wood. Part of this solution is mixed, under slight cooling, with fresh wood and the mixture charged into the head-container of the battery. After filling this, and allowing a few hours for reaction time, an amount of solution is drawn from this container, through the pressure of the incoming acid, which corresponds to the yield from one charge.

The solution drawn off contains hydrochloric acid and carbohydrates in about equal parts, and at a concentration of about 25 per cent (by weight) each. It is concentrated in stoneware tubes under vacuum. The distillate, containing about 80 per cent of the hydrochloric acid, with minor proportions of acetic acid and furfural, is reused after fortification. The concentrated sugar solution is dried to a powder in a spray-drier, where it also loses most of the remaining acid.

The dry, somewhat acid, powder contains the carbohydrates in the form of polymers. They are water-soluble and digestible; however, they must be

hydrolyzed for fermentation or crystallization of the monomeric sugars. This is done by dissolving, diluting to approximately 20 per cent sugar concentration, and heating for two hours, in the presence of 2 per cent acid, at 125° C. Part of the glucose can be crystallized from the neutralized and reconcentrated solution, while the mother liquors are fermented to alcohol or used for growing yeast.

When hardwoods are to be used it is necessary to remove a part of the hemicellulose first by prehydrolysis. This has been carried out in large scale only with straw, a substance similar to hardwood, by heating it in an 8 to 1 liquid to solid ratio, with 0.5 per cent sulfuric acid for 2 to 3 hours

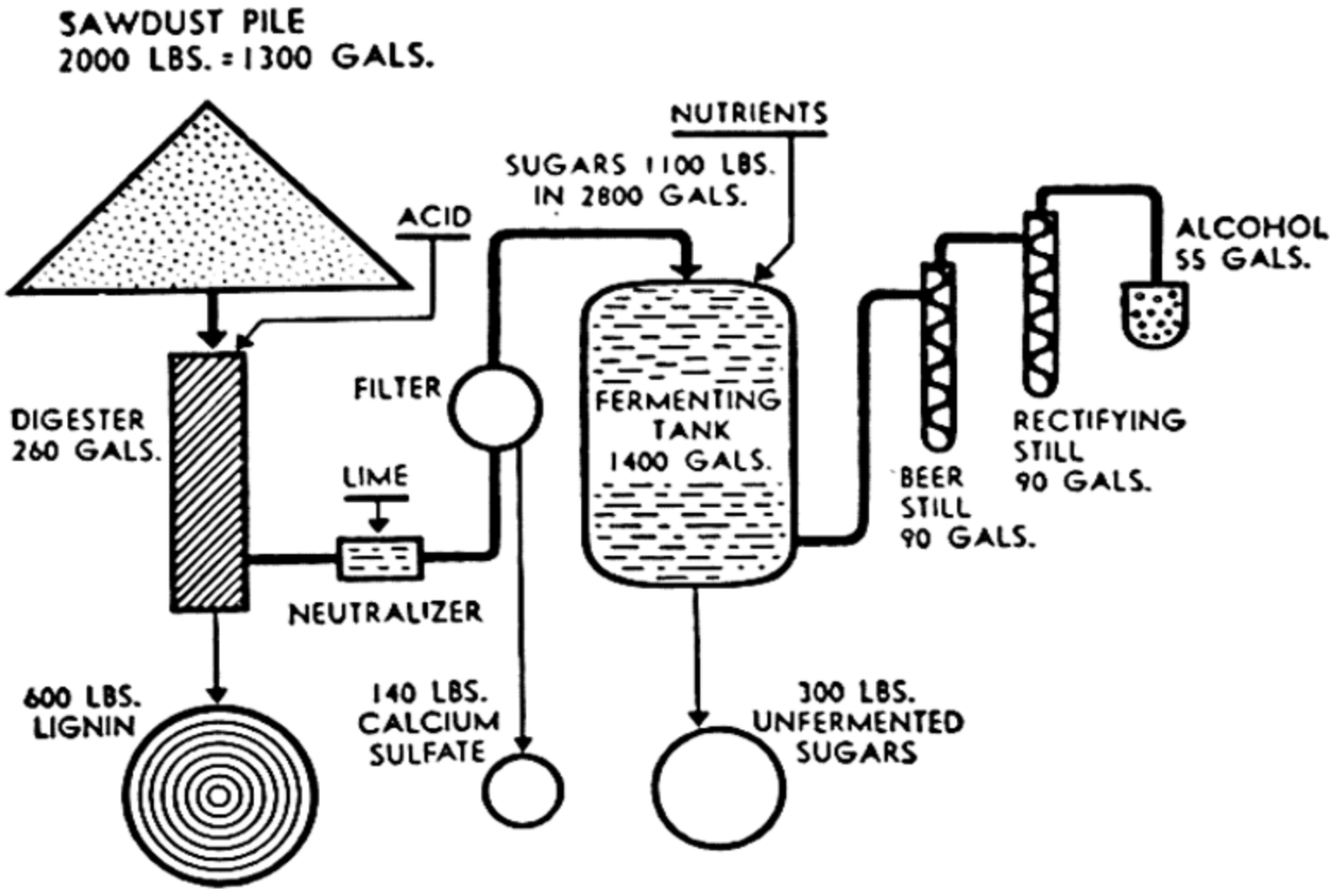


FIGURE 129.—Materials relation in the hydrolysis of wood by means of dilute mineral acid under pressure. (From "Chemical Economics of Wood Hydrolysis," E. Farber, *Chemurgic Digest*, March 31, 1945.)

at 130° C. (266° F.). Without prehydrolysis, hardwoods form slimy materials from lignin and pentoses which prevent passage of the hydrolyzing acid.

Madison Process with Continuous Percolation. In the Madison process, dilute sulfuric acid with an average concentration of 0.5 per cent is pressed through wood in the form of sawdust and shavings. Regular flow of the acid, and hence of the resulting sugar solution, is one of the two principal requirements; the other is a lignin residue which can be discharged from the pressure vessels without manual labor. Both depend upon careful charging of the wood, which should not contain too many very fine particles, and upon maintaining a pressure differential of not more than 5 to 6 lbs./sq. in. between top and bottom of the digester. The digesters or percolators are hydrolyzing vessels under pressure, such as 150 lbs./sq. in., with a capacity of 2000 cubic feet each.

In the original Scholler plants in Germany, they are lined with lead and acid-proof brick; in the Oregon plant, a lining of "Everdur" metal gives sufficient protection. The wood, about 15 tons, is pressed down with steam,

and then heated by direct steam, after which the acid is introduced. The practice in Germany was to bring the dilute acid into the digester in several batches, with rest periods of about 30 minutes, heating the wood to temperatures of 130° C. (266° F.) at first, then to 180° C. (356° F.), and keeping the temperature of the entering acid 10 to 20° C. lower. A total of about 14 hours was required to exhaust the wood, yielding about 50 pounds of carbohydrates for 100 pounds of dry wood substance. In the Madison process, continuous flow of the acid, and correspondingly, of the sugar solution, is provided—in other words, continuous percolation. The cycle is thereby reduced to 6 hours, and the yields are increased somewhat.

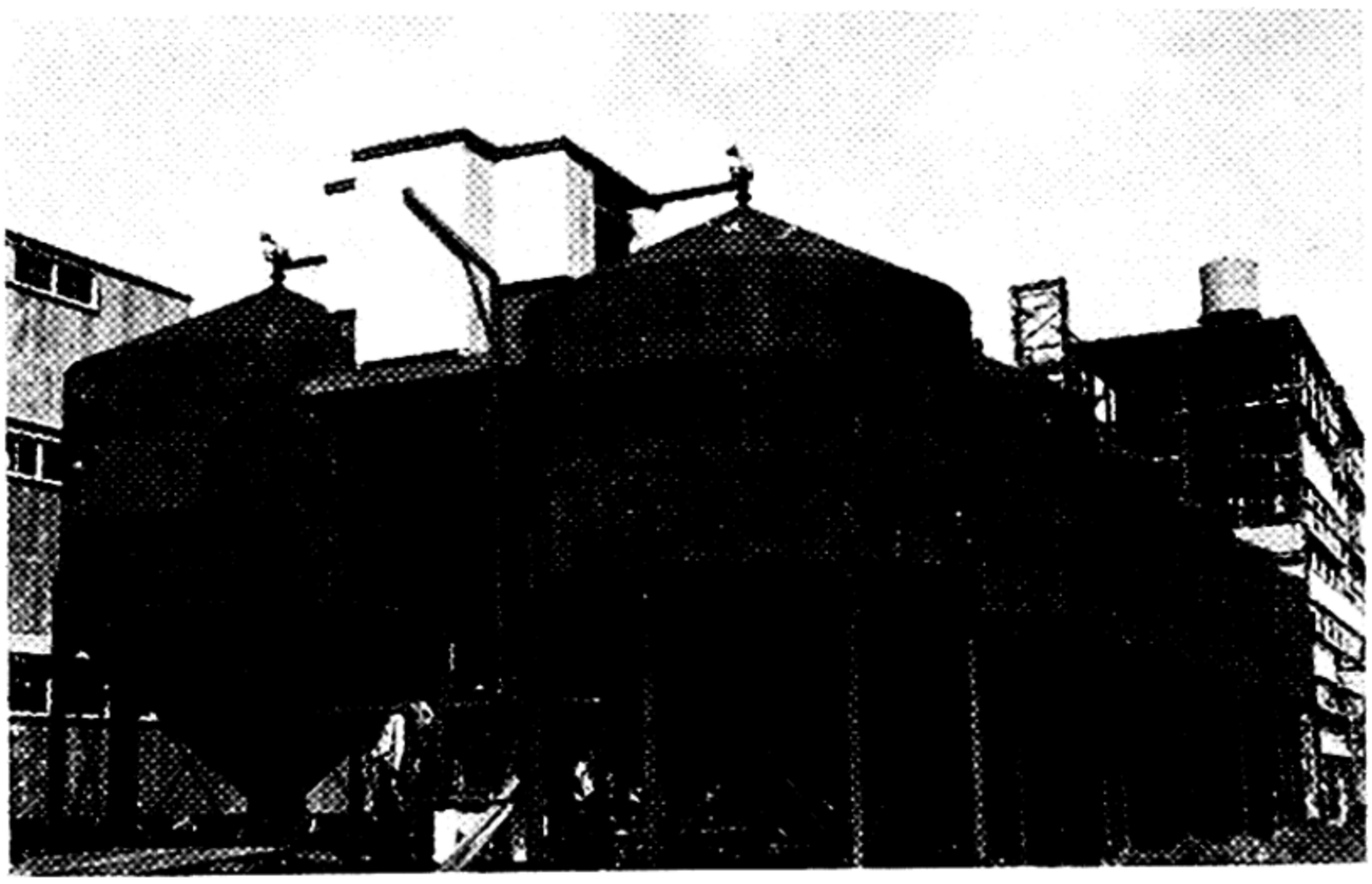


FIGURE 130.—General exterior view of still fermenter tanks in the Willamette plant for making ethyl alcohol from wood waste, "Plancor 2179." (Courtesy of Reconstruction Finance Corporation.)

The lignin is blown out of the digester by opening the specially constructed bottom valves while the vessel is still under pressure.

The sugar solutions usually contain about 5 per cent of carbohydrates and 0.5 per cent of sulfuric acid. The solutions, still under pressure (150 lbs./sq. in.), are flash-evaporated to 35 lbs./sq. in., neutralized with lime at that pressure, and filtered. Calcium sulfate is much less soluble at the elevated temperature corresponding to the pressure than it is at 100° C. This is a fortunate circumstance, for it must be removed to an extent sufficient so that it will not cause difficulties by forming incrustations in the subsequent alcohol distillation. The filtered solution is cooled by further evaporation (flash) and heat exchange with water to fermentation temperature. Alcohol (ethyl) yields of over 60 gallons per ton of dry wood have been obtained from the pilot plant. It is expected that in this plant, alcohol (ethyl alcohol 95 per cent) can be produced at a cost of 40 cents per gallon.

Comparison. In the Bergius-Rheinau process the concentrated hydrochloric acid employed requires dried wood, and recovery of the acid is essen-

tial. The process gives high yields of sugars (60 to 65 per cent) at high concentrations. The sugars first obtained, however, call for an extra processing step to reduce them to monomers, before fermentation and crystallization. All in all, the process is too expensive for general use in its present form. The dilute sulfuric acid employed in the Madison process gives lower yields (50 to 55 per cent) of sugars, and only very dilute solutions are obtained directly. The difference in yield is not important with a low-cost material like wood waste. Recovery of heat is easier in this process and the acid need not be recovered. For these various reasons, the Madison process is more economical and is the one preferred in this country.

The plant in the Willamette valley (Springfield, Oregon), is still owned by the Defense Plant Corporation; it is for sale (April, 1948), or it may be leased.

Distillation

The development of wood distillation from the old practice of making charcoal by the slow burning of a pile covered by earth to the use of retorts with extensive recovery of distillates was related, in its early phases, to the expansion of the iron industry. About 150 years ago recovery of distillates was restricted to acetic acid and its salts. Methanol (CH_3OH) acetone ($CH_3 \cdot CO \cdot CH_3$) from pyroligneous acid, and guaiacol, ($C_6H_4 \cdot OH \cdot OCH_3$) from the tar were later added to the products of distillation. More recently attention has been given to chemicals present in small quantities, like acetol acetate, the ester of oxy-acetone, and maltol, a pyrone derivative. Such new chemical products, and improved engineering for better control, reduction of heat losses, and continuous operation with recycling of gas, coupled with the insistent demand for charcoal, will keep an industry alive which seemed about to die out because of successfully competing synthetic production of methanol, acetone and acetic acid.

Methanol is a good solvent for gums, shellac and other resins, besides being used as a denaturant for ethyl alcohol and in antifreeze compositions. Formaldehyde is an important product of its oxidation. Acetic acid and its anhydride find a large market in the field of cellulose acetate manufacture.

In the 18 months period from January 1, 1944 to June 30, 1945, a period within World War II, 444,100 tons of wood charcoal were allocated as follows:

	short tons*
Metallurgy and mining	217,068
Carbon bisulfide	69,553
General domestic	23,299
Activated carbon	18,097
Railroad dining cars	11,668
Black powder	10,091
Acetylene gas cylinders	5,842
Glass	1,398
and many other industries	

* "Facts for Industry."

The activity in the industry in years since then has remained high, although somewhat below that of the war years, as shown by the production

of methanol or wood spirits. On a 100 per cent methanol basis, the production in 1944 was 3,357,000 gallons, in 1945 2,819,000 gallons, in 1946 2,366,000 gallons, in 1947 2,530,000 gallons. For comparison, the synthetic alcohol produced in 1946 was 74,148,000 gallons.[4]

The total capacity of the hardwood distillation plants in this country at present (1948) is 1377 cords per day. Canada, Sweden, Norway and Germany have extensive wood distillation industries.

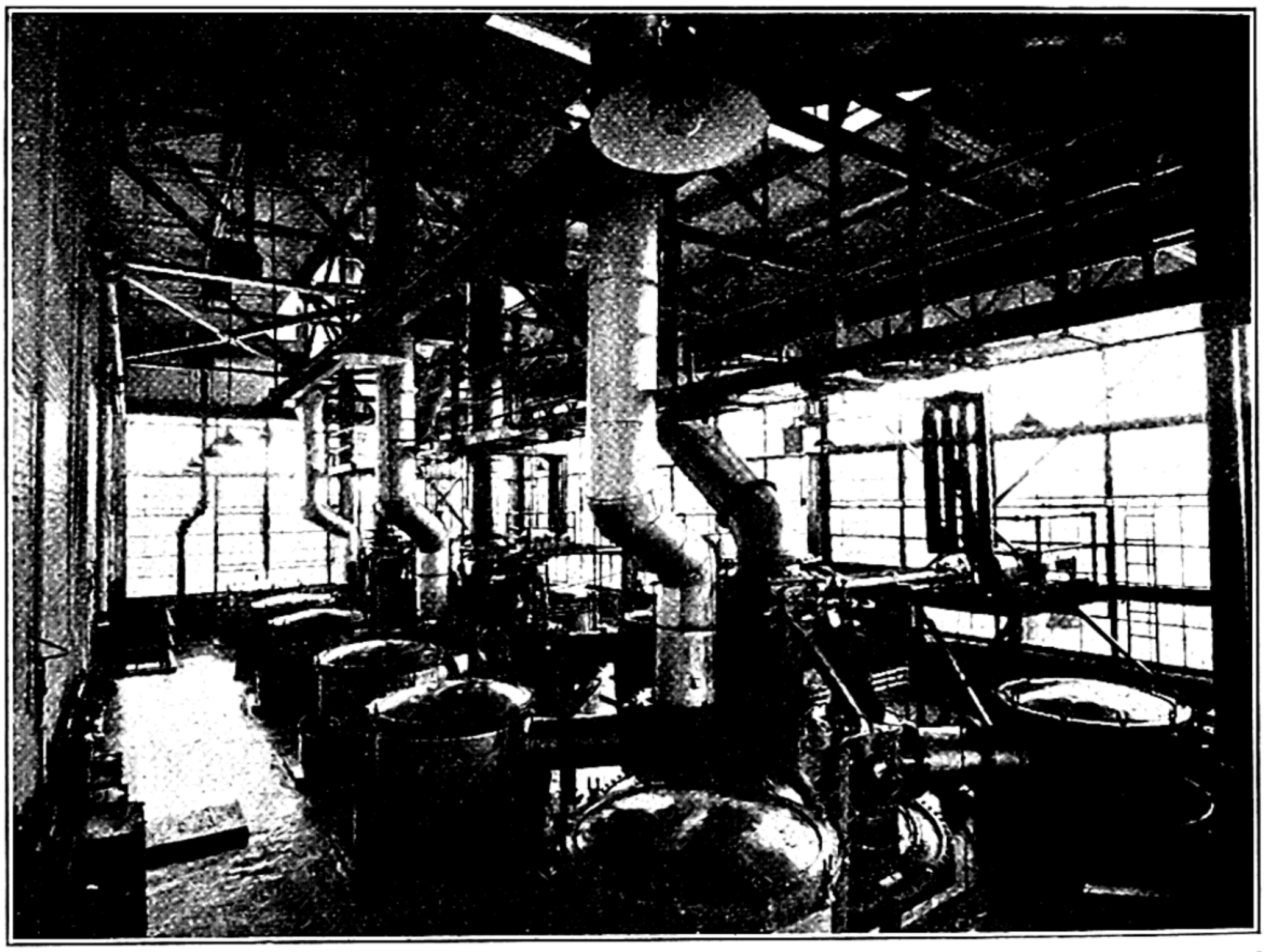


FIGURE 131.—Operating floor of the retort department. The top of the Stafford retorts (3) are flush with the floor; around each retort, four condensers are grouped. Each retort has a feed pipe terminating in a motor-driven barrel valve. The pipe with the offset leading out of each retort is for the fire-gases during preheating period. (Courtesy of the Ford Motor Company, Dearborn, Mich.)

Retort with Steel Buggies. In the older practice, 2 cords of air-dried wood (beech, maple, oak, hickory) cut in 4-foot lengths, are piled on a steel buggy; four buggies are pushed into a retort, 55 feet long, which they just fill. The retort is made of steel, with an outer brick shape which leaves a space around the sides and top in which the fire gases circulate. The doors are closed, and heat applied by burning natural gas or oil. Two openings in the rear wall allow the volatile products to pass out.

The cycle is 24 hours; during the first few hours, the heating is rapid, in order to reach the distillation temperature; water comes over first. An exothermic reaction takes place next, when the outside heat must be decreased; the vapors pass out to the condenser to form there the liquid condensate, the pyroligneous acid; the uncondensed gas is piped to the

[4] Industrial Reference Service, July 1947, part 12. Dept. Commerce.

boiler house. After about 10 hours, the flames in the burners are raised again, but not as high as at first. After 22 hours, the distillation is over; all burners are turned off, and the retort is allowed to cool for 2 hours.

The buggies are placed in air-tight cooling chambers for two days, with a quenching spray of water after the first day. The charge shrinks considerably during the distillation, but the charcoal is obtained in the form of rather large pieces, and very little dust.

The pyroligneous acid is first neutralized with lime, and then distilled, to give overhead a crude methyl alcohol, leaving the calcium acetate in the still. The operations described are performed in or near the forest lands. The crude methyl alcohol is shipped in car tanks to refineries which produce acetaldehyde, methyl alcohol, acetone, methyl ethyl ketone, methyl acetate, and other esters. The calcium acetate is first dried in pans with a rotating sweeper arm, producing the dry acetate in the form of large granules; the dry product is shipped to chemical concerns which treat it with mineral acid and distill the acetic acid.

This procedure is now obsolete; the more modern methods are described below.

A cord of seasoned wood weighs about 3000 lbs.; the charcoal produced is about 1000 lbs., and the amount of permanent gas 7000 to 9000 cubic feet.[5]

Retorts with Continuous Operation. The wood-distillation plant of the Ford Motor Company is a departure from the old practice not only in the acetic recovery method, but also in the retorts for distillation, which operate continuously. Still another difference is that the heat comes entirely from the exothermic reaction with which all wood distillers are familiar. A newly cleaned retort must be brought to the proper temperature by burning wood gas, but once the necessary temperature, 540° C. (1004° F.), has been reached, no external heat is needed. (See Figure 131.)

The plant was erected in order to utilize the scrap wood from the automobile (including station wagons) body plant; it was desired not to make acetic acid, but ethyl acetate, which the Ford Company requires in its lacquer and artificial leather departments.

The operation may be described as follows:[6] The scrap wood is reduced to small size (up to 8 inches by 2 inches by ¾ inch) in a hog mill, passed through a drier reducing moisture to 0.5%, and fed through barrel valves[7] at the top of Badger-Stafford retorts. These are vertical cylinders of steel, 10 feet wide by 40 feet high, with a heat-insulating inside wall 18 inches thick, composed of fire-brick, diatomaceous earth, and insulating brick. The heat developed by the exothermic reaction near the center of the retort rises with the vapors and gases developed, and warms the incom-

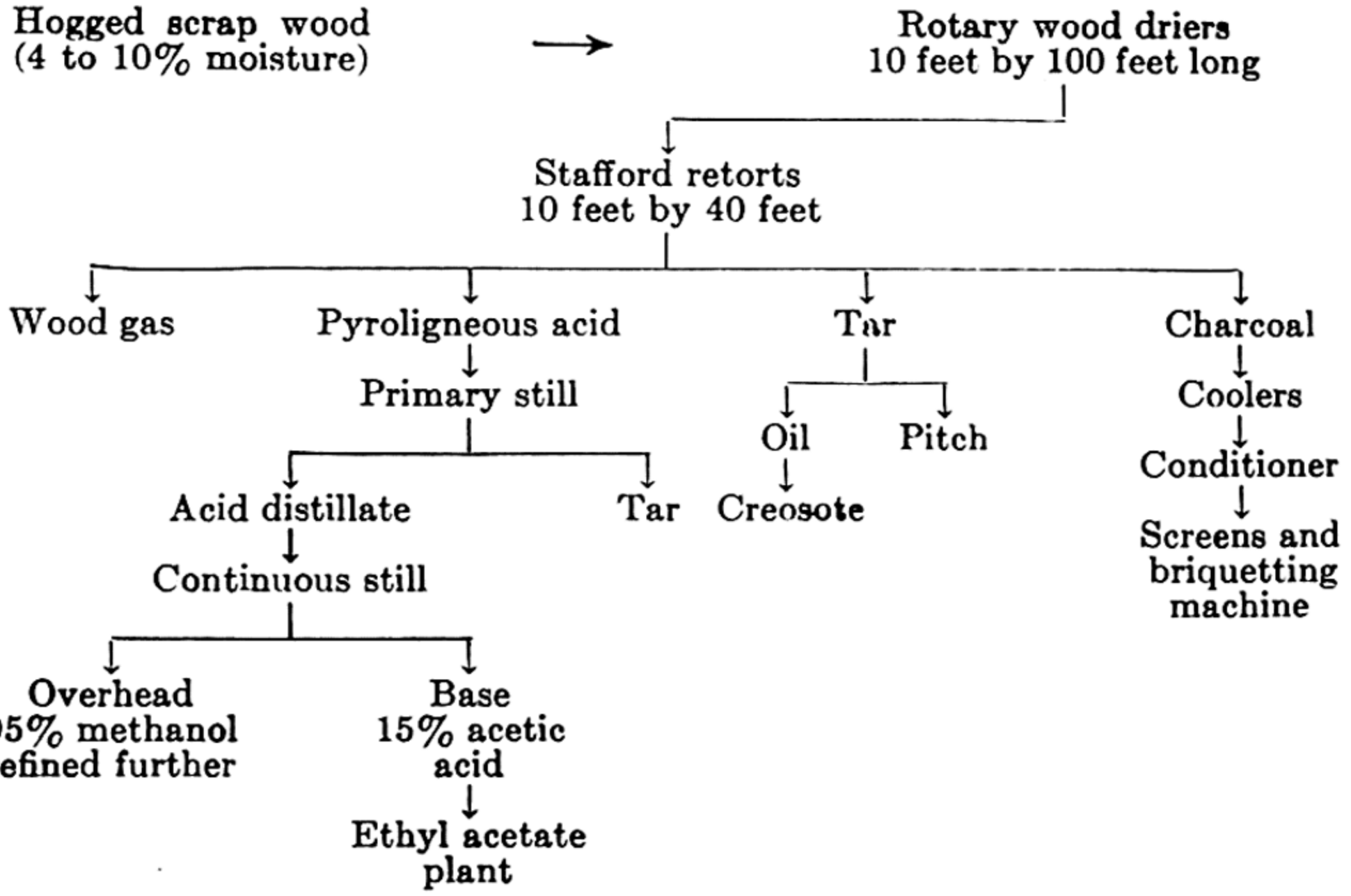
[5] A table will be found on p. 10 of "Distillation of hardwoods in Canada," by John S. Bates, Can. Dept. Interior, Forestry Branch, Bull. No. 74, Ottawa, 1922. See also "New products from wood carbonization," A. W. Goos, and A. A. Reiter, *Ind. Eng. Chem.*, 38, 132-5 (1946).

[6] From a description kindly furnished by the Ford Motor Company, and modified slightly, under date of March 1, 1948.

[7] A barrel valve may be said to consist of two barrels, one fitting inside the other, and the inner one free to rotate by turning on its axis; the inner barrel has two staves missing, so that the charge falls inside of it. By turning, the charge is dumped, while the vessel at the same time is sealed.

ing charge until it reaches the reaction temperature and itself distills. The average temperature in the center of the retort is 515° C. (950° F.) and near the bottom, 255° C. (490° F.). The carbonized material is discharged at the bottom through a barrel valve (Figure 132). The charcoal drops into a cooler 6 feet in diameter and 30 feet long, cooled by water coils and a trickle of water on the outside. It passes next to the rotary conditioner, where it absorbs oxygen; the heat of absorption is dissipated by cooling water over the outer walls. It is now ready for screening and briquetting. The conditioning takes 5 hours, instead of 48 hours in the standard buggy coolers.

Flow sheet for the Ford continuous wood distillation plant, Iron Mountain, Mich.



The gases and vapors passing out of the retort are cooled, the condensed pyroligneous acid is stored, the gas is scrubbed and blown to the power house, where it is burned under boilers, except the part used to bring a fresh retort to the proper temperature.

After operating two weeks, a retort must be taken off the line, and the accumulated tar burned out; it is then brought up to temperature by burning wood gas in it for 24 hours.

The pyroligneous acid is settled and distilled from batch primary stills to remove dissolved tar. The acid distillate then goes to a continuous still, which gives overhead 95 per cent methanol, and at the base 15 per cent acetic acid.

The methanol is refined in two discontinuous stills, with the production of denaturing grade methanol, various types of methanol antifreeze and C.P. methanol.

The 15 per cent acetic acid is treated with ethyl alcohol in the presence of sulfuric acid to give a crude ethyl acetate. The crude is washed to

remove excess alcohol and to increase the ester content. The washed crude is then azeotropically distilled, resulting in wet ethyl formate as heads product, 99 per cent ethyl acetate as main product, ethyl propionate forming the tails product. The average yield of the various products is given

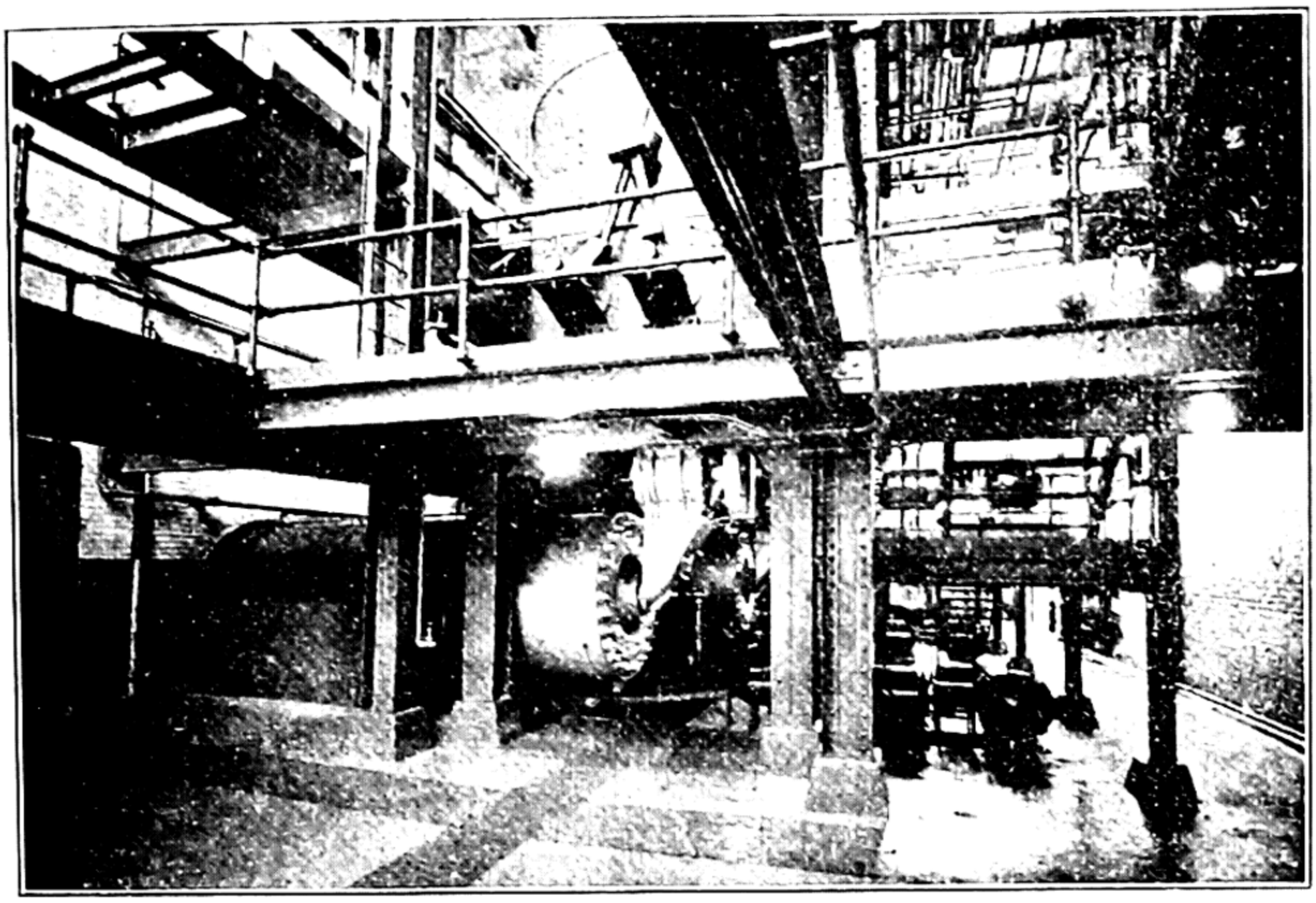


FIGURE 132.—First floor of retort department, showing the bottom and charcoal discharge end of the Stafford retort. The bars for shaking the grates are visible in upper center. The motor-driven barrel valve delivers the charcoal to the cooler, which extends beyond the wall to the left. The head of the second cooler is visible. (Courtesy of the Ford Motor Company, Dearborn, Mich.)

in Table 49. For the present, the wood tar is not distilled for the production of pitch and creosote oil, as is usually done, but is used as fuel in the powerhouse.

The wood used is 70 per cent maple, 25 per cent birch, and 5 per cent ash, elm and oak. The plant is designed for a capacity per day of 400 tons of scrap wood.

TABLE 49.—*Average yield of various products at the Iron Mountain Plant, Ford Motor Company, per ton of dry wood.*

Charcoal	649 pounds
Gas	5000 cubic feet
C. P. methanol	3.66 gallons
Methyl acetone (and methyl acetate)	1.46 gallons
Allyl alcohol	.05 gallon
Ketones	.30 gallon
Methyl acetate	0.945 gallon
Soluble tar	37.46 gallons
Pitch	66.0 pounds
Creosote oil	3.25 gallons
Ethyl acetate	14.65 gallons
Ethyl formate	1.27 gallons

The average composition of the gas from the Badger-Stafford retorts is hydrogen 2.2 per cent by volume (dry gas); methane 16.8; C_nH_m 1.2; carbon monoxide 23.4; carbon dioxide 37.9; oxygen 2.4; nitrogen 16.0; Btu. per cubic foot 290.

A continuous process of wood distillation with a circulating gas furnace has been introduced in two plants in Switzerland, with good results. Plans to construct similar plants in the United States are viewed with favor.[8] In the furnace, the final carbonization temperature is approximately 520° F.,

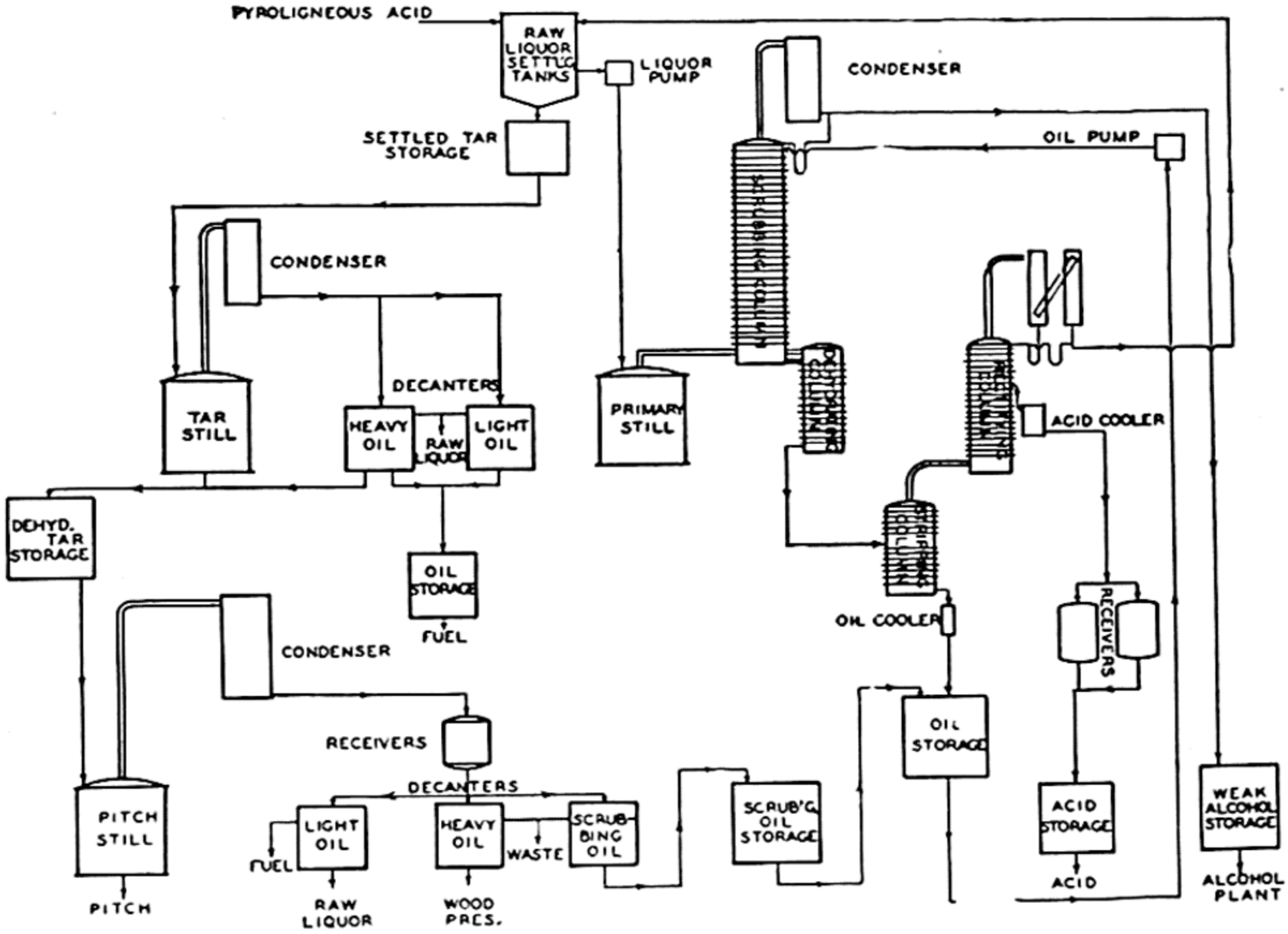


FIGURE 133.—Flow sheet of the original Suida process for the extraction of acetic acid directly from the pyroligneous acid vapors. The process has been slightly modified recently by the introduction of an additional column, the ethyl acetate column, between the stripping and rectifying columns (Dec., 1947). (Courtesy of Forest Products Chemical Company, Memphis, Tenn.)

at which point the exothermic reaction brings about a rise to between 830 and 1020° F. (443 and 604° C.). In order to control the temperature, steam may be introduced. The cycle is 16 to 20 hours.

DIRECT RECOVERY OF ACETIC ACID

In the early days, the plant in the mountains made its acetic acid transportable by changing it into calcium acetate, which involved neutralization with lime, and evaporating to dryness. The customer had to distill this acetate with sulfuric acid in order to obtain the free acid. The development of synthetic acetic acid made it economically impossible to continue this procedure; the wood distillation plants were the more pressed to reduce

[8] "The continuous processes of wood distillation," Robert S. Aries, *Chemurgic Digest* 4, 173 (June 15, 1947).

costs, in that synthetic methanol had cut the price of their second product, wood alcohol. Several processes have been invented and perfected by the users, in which the acetic acid is extracted from the acid distillate by means of solvents, with subsequent separation by distillation. The Brewster process uses isopropyl ether as the solvent; the Suida process uses a high-boiling wood-oil fraction, produced from the wood in the plant, and used over and over again for a reasonable number of cycles. The expense of buying a dissolving agent thus disappears in the Suida process, and an

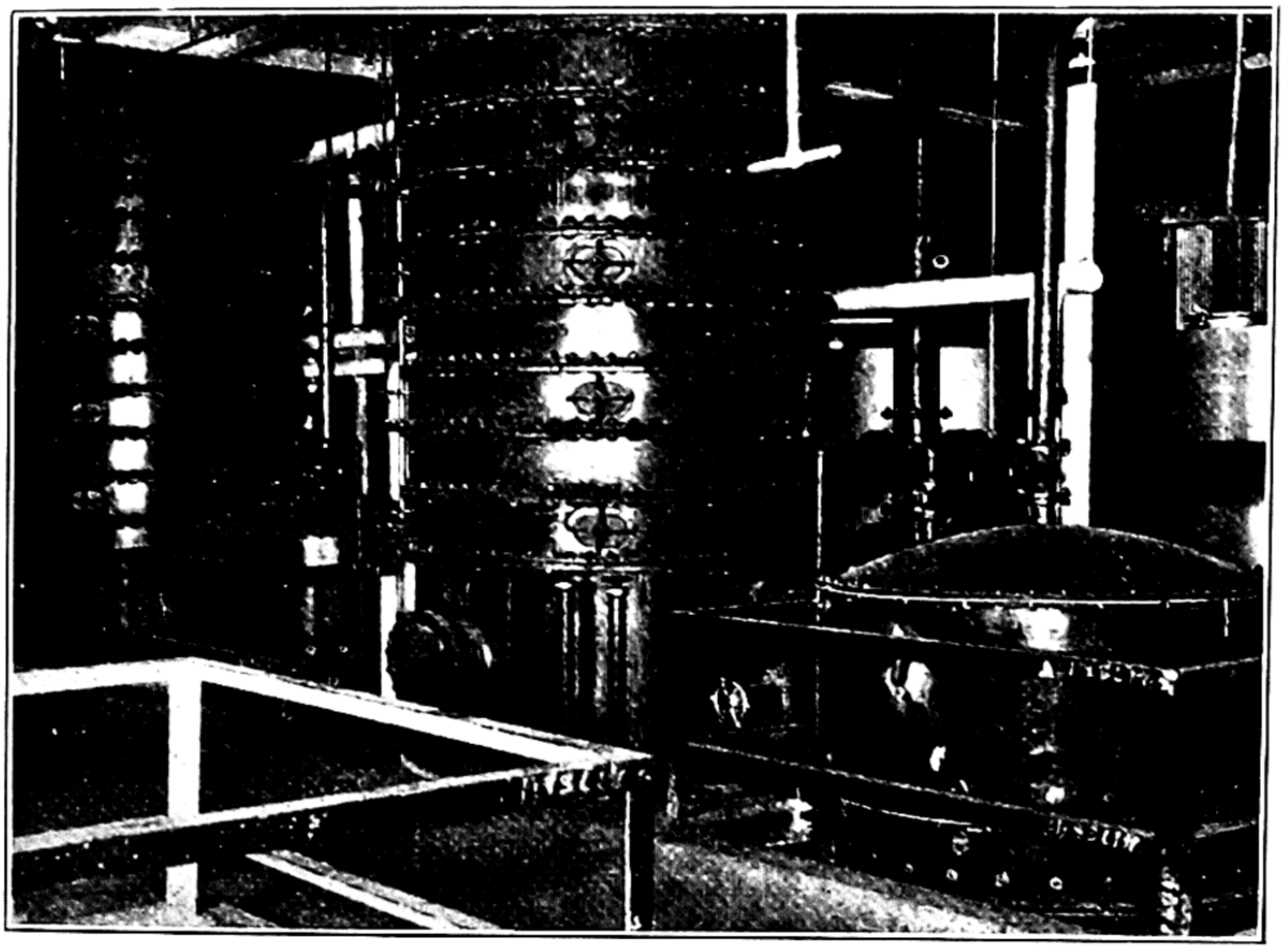


FIGURE 134.—The Suida process. Scrubbing columns, with the tops of the dehydrating columns shown. (Courtesy of Mr. T. C. Albin, Forest Products Chemical Co., Memphis, Tenn.)

acetic acid of 92 per cent strength is produced of high purity. The Brewster process, it might be added, is particularly applicable to the recovery of acetic acid in a cellulose acetate plant.

The Suida Process.[9] The apparatus, aside from retorts and the copper condensing equipment, includes a primary boiler, a scrubbing column, a dehydrating column, the second boiler, a stripping column (10 plates), a rectifying column (30 plates), a still for tar, and one for pitch, both with condensers and receivers. (See Figure 133.)

The extraction is carried out in the superheated vapor phase. The settled pyroligneous acid is run to the primary still, which sends out vapors of acetic acid, alcohol, and water, retaining the dissolved tar, which is

[9] "Acetic acid and cellulose acetate in the United States," E. P. Partridge, *Ind. Eng Chem.*, 23, 482 (1931); "Suida process for acetic acid recovery," E. P. Poste, *Ind. Eng Chem.*, 24, 722 (1932).

run off periodically. The heating is by closed steam coils, and the vessel and coils are of copper.

The vapors of acetic acid, crude methanol, and water enter at the base of a plate column, called the scrubbing column. (See Figure 134.) Solvent oil enters near the top of the column and flows downward, while the vapors pass upward. The solvent oil takes up acetic acid vapors and some water. Solvent oil charged with acetic acid and some water is drawn from the base of the tower; crude methyl alcohol, aldehydes, and water pass out of the column at the top. This overhead distillate is condensed and, for the most part, run to the weak alcohol storage; a small amount is returned to the still as reflux. The oil with acetic acid passes down the dehydrating tower, and from there to the second boiler (not shown on flow sheet), which delivers the heated liquid to the stripping tower, operated under vacuum. Here the acetic acid vapors are flashed off (that is, vaporized with explosive violence) and enter the rectifying column, carrying a small amount of oil with them and all the water present. The lower part of the stripping column serves to exhaust the oil of acetic acid. In the rectifying column, the oil is retained on the first few plates, and acetic acid of 92 per cent CH_3COOH is drawn off from the twelfth plate from the bottom. The upper 18 plates receive most of the water which entered the rectifying tower; they carry an acetic acid solution which becomes gradually weaker. There passes out at the top a 15 per cent acetic acid which is condensed and returned, mainly to the pyroligneous storage.

The solvent oil leaves the stripping tower free from acid; it is cooled and returned to the scrubbing tower. It is obtained in the first place as follows: the tar is distilled and the distillate gives a light oil, and a heavy oil fraction. The latter is placed in the tar still, and distilled again. The distillate is divided into light oil, heavy oil, and scrubbing oil; it is the last fraction which serves as solvent. The excess is sold or burned as fuel.

In a third process [10] for direct acetic acid, a "withdrawing agent" such as ethylene chloride or butyl alcohol, is added; an azeotropic mixture distills over water being one of its components. On cooling the vapors, the "withdrawing agent" forms a separate layer so that it is readily recovered and used over again. The acetic acid, free from water, is left in the bottom of the still.

Several additional observations are in order. As modified in the American practice, the methanol need not be removed in a preliminary distillation of the pyroligneous acid; distilling the alcohol simultaneously with the removal of acetic acid by the solvent reduces by half the amount of esters formed; to that extent the alcohol as such is preserved, and also the acid. A plant which finds the production of calcium acetate no longer profitable can be changed into a Suida plant, using the same retorts. Pure acetone formerly was made exclusively by the distillation of calcium acetate; it is now obtained by fermentation or by synthesis. (See pages 325, 410, and 413.)

In 1946, the production of natural acetic acid was 27,767,000 pounds;

[10] U. S. Patents 1,804,745 and 1,917,391. *See* further: *Chem. Met. Eng.*, 40, 631 (1933); and 41, 81 (1934).

recovered acetic acid amounted to about 1200 million pounds, while synthetic acetic acid reached the figure of 285,452,000 pounds. All these figures are for 100 per cent acid.

Refining the Alcohol. The crude alcohol fraction is separated into a number of purer substances in a continuous distillation with plate towers, similar to the procedure used for ethyl alcohol, fully described in Chapter 20. In a crude containing 82 per cent organic substances, there are 6 to 8 per cent of methyl acetate, $CH_3 \cdot COOCH_3$, 12 to 14 per cent of acetone, 65 per cent of methanol, and not over 1 per cent of other organic bodies such as allyl alcohol, $CH_2 : CH \cdot CH_2OH$, and methyl ethyl ketone $CH_3 \cdot CO \cdot C_2H_5$. The separation is mainly in four grades: acetaldehyde, boiling at 20° C. (68° F.); acetone with 28 per cent methyl acetate, 51 per cent acetone, and 21 per cent hydrous methanol, used as an excellent solvent for nitrocellulose under the name of "methyl acetone"[11]; a high-test methanol, and the allyl compounds.

Acetaldehyde may be transformed into paraldehyde, a polymer $(CH_3 \cdot CHO)_2$, by the action of a small amount of concentrated sulfuric acid. Paraldehyde is a liquid boiling at 128° C. (262° F.); it is a valuable hypnotic.

Acetone. The oldest commercial method for making acetone, in addition to that obtained from crude methanol, is the decomposition of calcium acetate.

$$\underset{\text{calcium acetate (a solid)}}{(CH_3 \cdot COO)_2Ca} \rightarrow \underset{\text{acetone (a liquid)}}{CH_3 \cdot CO \cdot CH_3} + CaCO_3$$

Acetone boils at 56° C. (133° F.). Until about ten years ago, the main source of acetone was the fermentation of starch, with butyl alcohol as a second product. Today, petrochemical acetone dominates the scene; such acetone is made from isopropyl alcohol by oxidative dehydrogenation. Isopropyl alcohol is made from propylene by catalytic hydration.

$$\underset{\text{propylene (a gas)}}{CH_2 : CH \cdot CH_3} + H_2O \rightarrow \underset{\text{isopropyl alcohol (a liquid)}}{CH_3 \cdot CH(OH) \cdot CH_3}$$

$$CH_3 \cdot CH(OH) \cdot CH_3 + \tfrac{1}{2}O_2 \rightarrow \underset{\text{acetone}}{CH_3 \cdot CO \cdot CH_3} + H_2O$$

*Production of acetone (in pounds).**

	1945	Unit Value
by fermentation	42,417,000	$0.07
from isopropyl alcohol	307,363,000	

* U. S. Tariff Commission.

Acetic Anhydride. The remarkable growth of the cellulose acetate industry has brought about a no less remarkable demand for acetic anhydride, one of the raw materials required. A number of novel methods have been developed and successfully launched. The older method which required sodium acetate, sulfur chloride and chlorine is now obsolete.[12]

[11] Acetone is not isolated as such from crude wood spirits; methyl acetate and acetone form a constant boiling mixture.

[12] German Patent 273,101, an improvement on 222,236, 241,898 and 132,605. Also see the Fourth Edition of this book.

Acetic anhydride is made at the present time by four or five methods. In one of them, ethyl alcohol (95 per cent) is catalytically dehydrogenated to acetaldehyde, which is oxidized to acetic acid (see Chapter 25). The acetic acid is concentrated to glacial strength, and this latter transformed into acetic anhydride and water by thermal cracking. The two products are rapidly separated. In a German process, the catalytic dehydration of the glacial acetic acid takes place with the latter in the vapor state, and while accompanied by the vapors of triethyl phosphate as catalyst.[13] In another variation of the same process, temperatures of between 500 and 1000° C. are mentioned, with the aid of activated charcoal, aluminum oxide, or phosphoric acid.[14] Another process now in operation is the reaction of ketene with acetic acid.[15]

$$\underset{\substack{\textit{ketene}\\(\text{a gas})}}{CH_2{:}CO} + \underset{\substack{\textit{acetic}\\\textit{acid}}}{CH_3COOH} \rightarrow \underset{\substack{\textit{acetic}\\\textit{anhydride}}}{CH_3{\cdot}CO{\cdot}O{\cdot}OC{\cdot}CH_3}$$

Ketene is made by the thermal decomposition of acetone,[16] and also from acetic acid by deep dehydration. In still another process acetylene is reacted with acetic acid, and the resultant ethylidene diacetate is decomposed by heat, yielding acetic anhydride and acetaldehyde; the latter is used in the acetic acid manufacture.[17] (More fully described in Chapter 25.)

$$2CH_3COOH + C_2H_2 \rightarrow \underset{\textit{ethylidene diacetate}}{(CH_3COO)_2{:}CH{\cdot}CH_3}$$

$$(CH_3COO)_2{:}CH{\cdot}CH_3 \xrightarrow{\text{heat}} (CH_3CO)_2O + OHC{\cdot}CH_3$$

Finally, in the Shawinigan process, acetaldehyde is oxidized in the presence of a diluent to peracetic acid which on further reaction with acetaldehyde gives acetic anhydride and water. The latter two are separated by distillation at low pressure.[17]

$$CH_3CHO + O_2 \rightarrow \underset{\textit{peracetic acid}}{CH_3CO{\cdot}O{\cdot}OH}$$

$$CH_3CO{\cdot}O{\cdot}OH + CH_3CHO \rightarrow (CH_3CO)_2O + H_2O$$

Acetic anhydride boils at 138° C., while glacial acetic acid boils at 119° C. Preferably, the anhydride is distilled or redistilled at reduced pressure. The production of acetic anhydride from all sources was 524,748,000 pounds in 1945. In 1949, it is expected that 850,000,000 pounds will be produced.

Other Patents

U. S. Patent 1,792,392, on turpentine, pine oil and rosin from wood rich in oleoresin by the direct action of strong current of steam to volatilize the oils; 1,772,895, turpentine substitute from pine oil, by adding fuller's earth to pine oil and distilling with steam at a temperature of 125° to 225° C.; 1,740,115, extraction of turpentine pine oil and rosin from resinous woods, by solvents; 1,859,292, thermal decomposition of wood by subjecting it to direct physical contact and reaction with a highly heated

[13] *Chem. Met. Eng.*, 53, Feb. 1946, p. 220.
[14] U. S. Pat. 2,249,527 (1941); 2,278,537 (1942).
[15] *Petr. Ref.*, 25, 611 (1946).
[16] U. S. Pat. 2,080,562.
[17] *Chem. Industries*, 63, 217 (1948).

body of hydrocarbons; 1,836,305, wood distillation apparatus; 1,731,242, method of wood distillation; 2,050,235, concentrating acetic acid; 2,034,332, concentrating aqueous formic acid; 2,177,557, distillation of wood chips.

Extraction:

Swedish No. 91,041 (K. F. Wilhelm, 1936) and German No. 716,939 (Stockholz Verwertungsges., 1942): turpentine vapors for extracting the resins; U. S. No. 2,424,628 (Robert C. Palmer, 1947): Dry wood is extracted with a mixture of petroleum solvent and alcohol containing water; U. S. No. 2,200,468 (F. J. Cirves, 1940): Recovering the soap from black liquor by demulsifying with air; U. S. No. 2,174,651 (R. J. Byrkit, Jr., 1939): Hydrogenation of rosin or rosin esters by continuously passing the liquefied material with hydrogen under pressure through catalyst beds; U. S. No. 2,228,365 (W. Reppe and W. Wolff, 1941): Vinyl esters from tall oil and acetylene by reaction at about 200° C., in the presence of zinc salt, and at atmospheric pressure.

Hydrolysis:

Bergius-Rheinau process: U. S. Nos. 1,544,149 (E. Hägglund, 1925); 1,863,654 (E. Farber, 1932); 1,969,600 (E. Farber and F. Koch, 1934). British No. 386,927 (Holzhydrolyse A. G., E. Farber, F. Koch and H. Specht). Scholler-Tornesch process: H. Scholler et al., U. S. Nos. 2,083,348 (1937); 2,188,192/3 (1940); German No. 644,500 (1937). U. S. No. 2,305,738 (F. Scheuing, 1942): Levulinic acid from wood by pressure heating with acid.

Distillation:

U. S. Nos. 2,202,231 (Theophil Reichert, 1940): Retort with conical top and bottom in which wood is heated with recirculated gases to maintain uniform temperatures between 500 and 750° C.; 2,289,917 (Auguste Lambiotte, 1942): Continuous carbonization with hot gases (300 to 600° C.) introduced into carbonization zone and cool gases (40° C.) at the discharge end; 2,395,010 (Donald F. Othmer, 1946): Amyl-acetate is used to entrain water from dilute acetic acid, by azeotropic distillation; 2,400,466, and 2,401,274 (A. A. Reiter and F. L. Bemen, 1946): Separation of methyl-cyclopentenelone and acetol-acetate from distillates.

Conversion of wood by resinification:

U. S. Nos. 1,797,559 (Orland R. Sweeney, 1931); 2,221,779 (William R. Collings, et al., 1940); 2,312,807 (E. Farber, 1943).

Hydrogenating the lignin in wood:

2,328,749 (Earl C. Sherrard and Elwin E. Harris, 1943).

Problems

1. When wood is hydrolyzed by means of sulfuric acid of 0.5 per cent concentration, carbohydrate solutions averaging 5 per cent in sugar content are produced. How much $CaSO_4$ is obtained, per ton of wood, on neutralization?

Answer: 190.8 pounds $CaSO_4$.

2. An average yield of alcohol from the fermentation of wheat (after conversion of the starch, and besides the by-products in stillage and "distillers grains") is 2.5 gallons per bushel (=60 lbs.). How much wood has to be hydrolyzed to give this amount of alcohol?

Answer: 83⅓ lbs.

3. A plant using retorts with steel buggies distills 30 cords of beech wood a day for 100 days. What is the total tonnage of charcoal, and how much gas is available per day?

4. A plant distills every day 200 tons of chipped waste hardwood in continuous retorts. Consulting the table of products given in text, what are the amounts of each which are obtained? Make an allowance for the gas required for cleaning the retorts and bringing them up to heat.

5. The methoxyl (OCH_3)-content of White Oak is 5.12 per cent. If this were completely converted into methanol, how much more per ton than the actual yield would be obtained on distillation?

Answer: 82 pounds. (One gallon of methanol weighs 6.6 lbs.).

Reading References

1. "Wood Chemistry," edited by Louis E. Wise, New York, Reinhold Publishing Corporation, 1944.

"Longleaf Pine," W. G. Wahlenberg, Washington, D. C. (Charles Lathrop Pack Forestry Foundation, in cooperation with the Forest Service, U. S. Dept. of Agriculture), 1946.

"Purification of wood rosin," H. E. Kaiser and R. S. Hancock, *Ind. Eng. Chem.*, 22, 446 (1930).

"Composition and Fractionation of American steam-distilled wood turpentine," U. S. Dept. of Agriculture, Techn. Bull. No. 596, Washington, D. C., 1937.

"Gum Naval Stores Industry," Carl E. Ostrom and Keith W. Dorman, Chemurgic Reprint Series No. 29, Columbus, Ohio, 1945.

"Fused Metal Resinates," J. N. Borglin, P. R. Mosher and H. A. Elliot, *Ind. Eng. Chem.*, 36, 752 (1944).

"Naval Stores, 1919-1939," Dr. Eldon Van Romaine, *Chem. Ind.*, Sept., Oct., 1939.

2. "Die Herstellung von Zucker aus Holz und ähnlichen Naturstoffen," F. Bergius, E. Farber, and O. Jellinek, in: "Ergebnisse der angewandten Physikalischen Chemie," Vol. 1, Leipzig, 1931.

"Conversion of wood to carbohydrates," F. Bergius, *Ind. Eng. Chem.*, 29, 247 (1937).

"Production of wood sugar in Germany and its conversion to yeast and alcohol," J. F. Saeman, E. C. Locke and G. K. Dickerman, Joint Intelligence Objectives Agency, Washington, D. C., Fiat Final Report No. 499, Nov. 14, 1945.

"Scholler-Tornesch process," H. Scholler and H. Fink, Techn. Bur. of Percola, 1939.

"Madison wood sugar process," Elwin E. Harris and Edward Beglinger, *Ind. Eng. Chem.*, 38, 890 (1946).

3. "Wood Distillation," L. F. Hawley, New York Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1923.

"The Technology of Wood Distillation," M. Klar, translated by Alexander Rule, New York, D. Van Nostrand Co., 1925.

"Suida process for acetic acid recovery," E. P. Poste, *Ind. Eng. Chem.*, 24, 722 (1932).

"Charcoal production," E. L. Heermance, Bull. No. 10, Northeastern Wood Utilization Council, New Haven, Conn., 1946.

"Wood Distillation," Bull. No. 15, Northeastern Wood Utilization Council, New Haven, Conn., 1947.

"Hardwood Distillation Industry, Revised March 1947," U. S. Dept. of Agriculture, Madison, Wis., No. R738.

"New Products from wood carbonization," A. W. Goos and A. A. Reiter, *Ind. Eng. Chem.*, 38, 132 (1946).

"German charcoal activating processes," S. Hormats, U. S. Dept. of Commerce, Office of Technical Services, PB 23,852 (1945).

"Continuous wood distillation gives better, cheaper charcoal," Robert A. Aries, *Chem. Industries*, 60, 968 (1947).

"Lignin: An economic liability or a chemical asset?," Harry F. Lewis, *Chem. Eng. News*, 23, 1074-1080 (1945).

"Forestry and the utilization of waste wood and its products as fuel," Norman Clarke Jones, *Trans. Institution of Chemical Engineers (London)*, 22, 120 (1944).

"Nature of the Chemical Components of Wood," Tappi Monograph Series No. 6, New York, 1948.

The electric furnace is a comparatively modern device. Until its advent, the highest temperature commercially available was the white heat of a bed of coal burning under forced draft, which gave about 1500° C.; in the electric furnace, a temperature twice as high is readily obtainable. For comparison, the temperature of the sun's surface is estimated at 6200° C. That the high temperature of the electric furnace should have made possible the manufacture of products hitherto unknown, or known only in the natural state, is not surprising. Important among these are artificial graphite, silicon carbide, aluminum oxide, calcium carbide, and certain alloys.

Chapter 17

Products of the Electrothermal Furnace

There are three main types of electric furnaces: the arc furnace, the resistance furnace, and the induction furnace. In the arc furnace, the heat of the arc is utilized, with perhaps an electrical effect in the case of gases. In the resistance furnace, no arc is formed, but the electrical energy is entirely transformed into heat or thermal energy. If the material furnishing the resistance is the charge itself, the resistance furnace is said to have direct heating. If a material is added purposely for the sake of the resistance it furnishes, without being part of the reacting charge, the furnace is said to have indirect heating. The induction furnace is applied only to metals; it is based upon the fact, that if an alternating current of high frequency is passed through a coil of many turns (primary) in the center of which a soft iron core is situated, an alternating magnetic field is formed, and a single iron ring (secondary) placed in the field around the first coil and core will become red hot in a few minutes. In addition to these three types, some furnaces involve a combination of two types. Any of these furnaces may be termed electrothermal, for their value lies in the heat they furnish, and that heat has its source in electrical energy. The materials produced in the electrothermal furnace could not be made by means of heat from any other source; it is the high degree of heat which is essential. At the present time no other means for the production of such high temperatures is known. The size of the furnace does not matter; a small furnace a few inches in dimension is as truly an electric furnace as a large furnace for graphite, 30 feet long.

Artificial Graphite

Artificial graphite, a crystallized form of carbon, is made in an electrothermal furnace with direct heating. When coke is heated to the very high temperature which this furnace affords, a change takes place, at the end of which the ash is volatilized as well as any other ordinarily more volatile impurities, and there is left only carbon in the form of graphite. The ash functions as the graphitizing agent; it forms carbides with the coke; later the carbides decompose, and the carbon is left in the form of graphite. The heating must be done in the absence of air; this is accomplished by covering the heated material with a sand mixture.

Certain materials are added to the coke in order to produce shaped pieces, for example, electrodes for electric furnaces and for electrolytic cells; it is these electrodes particularly which have made this industry indispensable. Graphite is a good conductor of electricity; coke is a poor one.

Electrodes for Electric Furnaces

The raw materials for artificial graphite electrodes are: calcined petroleum coke, coal-tar pitch, and a petroleum distillate such as black summer oil. The preparation of the coke is an industry in itself. Today, the well

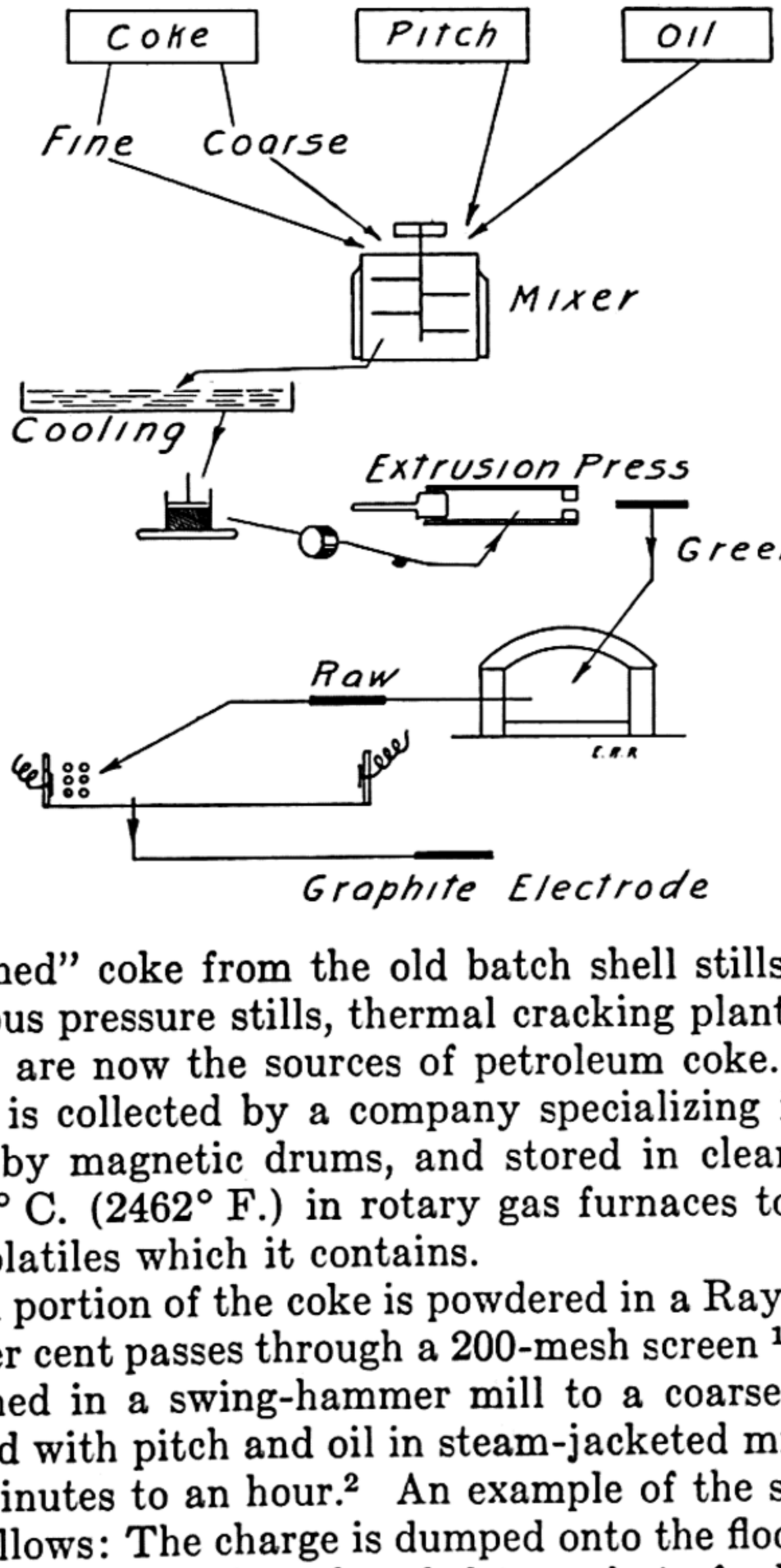


Figure 135.—Flow sheet for graphite electrode.

"burned" coke from the old batch shell stills is no longer obtainable: continuous pressure stills, thermal cracking plants and other petroleum refinery units are now the sources of petroleum coke. Such less perfectly "burned" coke is collected by a company specializing in this field, freed from tramp iron by magnetic drums, and stored in clean places. It is precalcined at 1350° C. (2462° F.) in rotary gas furnaces to remove the 20 per cent or so of volatiles which it contains.

A portion of the coke is powdered in a Raymond mill to such fineness that 60 per cent passes through a 200-mesh screen [1]; another portion of the coke is crushed in a swing-hammer mill to a coarse powder. These two sizes are mixed with pitch and oil in steam-jacketed mixers for a period varying from 20 minutes to an hour.[2] An example of the subsequent operations might be as follows: The charge is dumped onto the floor and allowed to cool to 95° C. (203° F.); it is then shoveled to a chute feeding a cylindrical form open at both ends, and placed upright on a movable table, so that the form may

[1] Chapter 44. The production of petroleum coke in 1945 was 2,023,000 tons; in 1946, 2,124,200 tons (U. S.).

[2] The different sizes of coke are used in order to obtain minimum voids.

be brought under a ram which presses the soft mass into a cake 16 inches in diameter and 10 inches high, weighing 60 to 70 pounds. The cakes are fed at intervals to an extrusion press, enough cakes being used to fill it. The press is merely a steam-jacketed cylinder of 17-inch internal bore, fitted at one end with a steam-heated die which may be changed to suit the order; at the other end with a hydraulically driven piston. The mass is extruded through the die, very slowly, onto a receiving plate. The diameter of the electrode is fixed by the die opening; the length is measured on a stick, and cut off with a wire, as cheese would be. Two men operate the extrusion end of the press; one operates the valves.

The pieces, now called the "green" electrodes, are lowered to the floor and rolled away in shallow troughs with 2 inches of water, and under a spray of cold water. By reason of this cooling, the soft mass becomes comparatively stiff; the green electrodes are now ready for firing. The amount of compression is reflected in the specific gravity: the 16-inch cake has a specific gravity of 1.3; the green electrode, 1.7.

First Baking, Producing Raw Electrodes. A first baking is done at a temperature of not over 1100° C. (2012° F.), producing a hard substance with a metallic ring. This may be done in the electric furnace, and may be followed without repacking by the graphitizing heat, merely by changing from a low transformer to a high one; but it is found more economical to perform the first baking in coal-fired kilns with removable arches. The kilns are of such size that for electrodes 4 inches in diameter (circular) and 40 inches long, 500 may be baked at one time in one kiln. The electrodes are packed in sand, preferably re-used sand, so that they do not touch each other, and are well covered so that the fire gases which pass over the top will not come in contact with them. The fire gases pass over the charge, down the sides and rear, and under the floor of the kiln by means of suitable channels and cross walls in the brickwork, before they can escape to the stack. A pyrometer [3] reaches into the sand; another is placed in the fire gases. The temperature is raised slowly, 5° C. per hour, requiring 5 to 7 days; when 800° C. (1472° F.) is reached, all danger of forming blow-holes is over and the fire is forced until the pyrometer in the sand registers 1100° C. (2012° F.); this heat is maintained for 2 to 3 days.

The charge is cooled slowly; first the arch is removed by an overhead traveling crane; after a day, some of the sand blanket is removed; on subsequent days more is removed until all the sand is finally taken off. The cold charge is unpacked, and the raw electrodes are ready for the graphitizing heat. The gradual cooling is necessary as the electrodes would take fire if air could reach them while they were still hot.

During the baking, there is a loss in weight of 13 per cent and a shrinkage in length of 1 per cent. The green electrode, 4 by 40 inches, weighs 29 pounds.

Carbon Electrodes

The raw electrodes are destined for the graphitizing furnace, although at this stage, they are already well suited for use in the electric furnace.

[3] Chapter 46.

Under the name of amorphous carbon electrodes, the product at this stage finds extensive use. The materials which serve for its preparation, however, are slightly different; they are a selected anthracite, carefully calcined, petroleum coke and tar or pitch as binder. Otherwise, the method of manufacture is as described under raw electrodes. The amorphous carbon electrodes, called "carbon electrodes," have a coarser structure than graphite electrodes; they may be machined, but less well. Similarly they conduct the current less readily, and heat more slowly than graphite electrodes. The specific electrical resistance in ohms per inch cube is 0.0003 to 0.0007 for the graphite electrode, against 0.0012 to 0.0042 for the amorphous carbon electrode. The thermal conductivity in gram calories per second per centimeter cube per ° C. is 0.176 for graphite, at 150-300° C. while for amorphous carbon electrodes it is 0.0086 to 0.020, at 175-675° C. The latter are cheaper, and have a higher crushing strength. Carbon electrodes with coal as base have from 4 to 10 per cent ash; if made from petroleum coke, 0.25 to 1.2 per cent; graphite electrodes have almost no ash (0.1 to 0.9 per cent). The carbon electrode leaves no mark on paper; a graphite rod leaves a black streak. A carbon rod has a metallic ring when dropped on a stone floor; the graphite rod has not.

Graphitizing the Raw Electrodes. The raw electrodes are changed from a hard body to one so soft that it may be cut with a pocket knife, in an electric furnace in which the charge itself forms the resistance to the passage of the electric current. The charge in the furnace reaches a temperature between 2500 and 3000° C. (4532 and 5432° F.), whereas the maximum heat which the coal-fired kiln affords is 1400° C. (2552° F.). The furnace consists of a bed of concrete flags supported on short piers placed close together, and of two upright end pieces, also of concrete. The length is 30 feet, from upright to upright; the width is 13 feet; there are no stationary side walls. When fully charged the height of the bed is about 6 feet.

The end pieces are provided with openings to receive the stationary graphite blocks forming the terminal electrodes for the furnace; each end piece has eight carbon blocks, 6 inches square in cross-section, long enough to protrude 2 inches within the furnace and to extend 6 inches outside for connection to the copper leads. The connection to the graphite terminals is kept cold by a stream of water.

The charge of raw electrodes is packed between the end pieces after placing ground coke over the floor of the furnace to a height of 4 inches; the electrodes are placed crosswise to the long axis of the furnace. They are piled exactly over each other, touching, and the vertical rows are separated by strips of wood, replaced by ground coke when the packing is completed. The total weight of the charge is 30,000 to 35,000 pounds. Along the two sides a layer of coke 3 inches thick is placed reaching from one upright end piece to the other; it is held in place temporarily by a sheet steel apron. A layer of coke is similarly placed over the top. It is through these layers that the current passes at the start, for the raw electrodes are poorer conductors than the coke. The graphite terminals in

the end walls are buried in the crushed coke and through it make contact with the electrodes nearest them.

Over the top a layer of mixed sand, coke, and sawdust is spread, to act as a heat-retaining cover; sand previously used, partly converted to silicon carbide, is preferred to new sand. Along the sides concrete blocks 4 feet high are set up at a distance of 12 inches from the 3-inch coke layer, and the space so formed is filled with used sand. The electrodes are now buried in crushed coke and protected from the air on all sides; the furnace is ready for the heat.

The current at Niagara Falls is 25-cycle [4] alternating current; the voltage at the beginning is 240 volts; as the heating progresses the charge

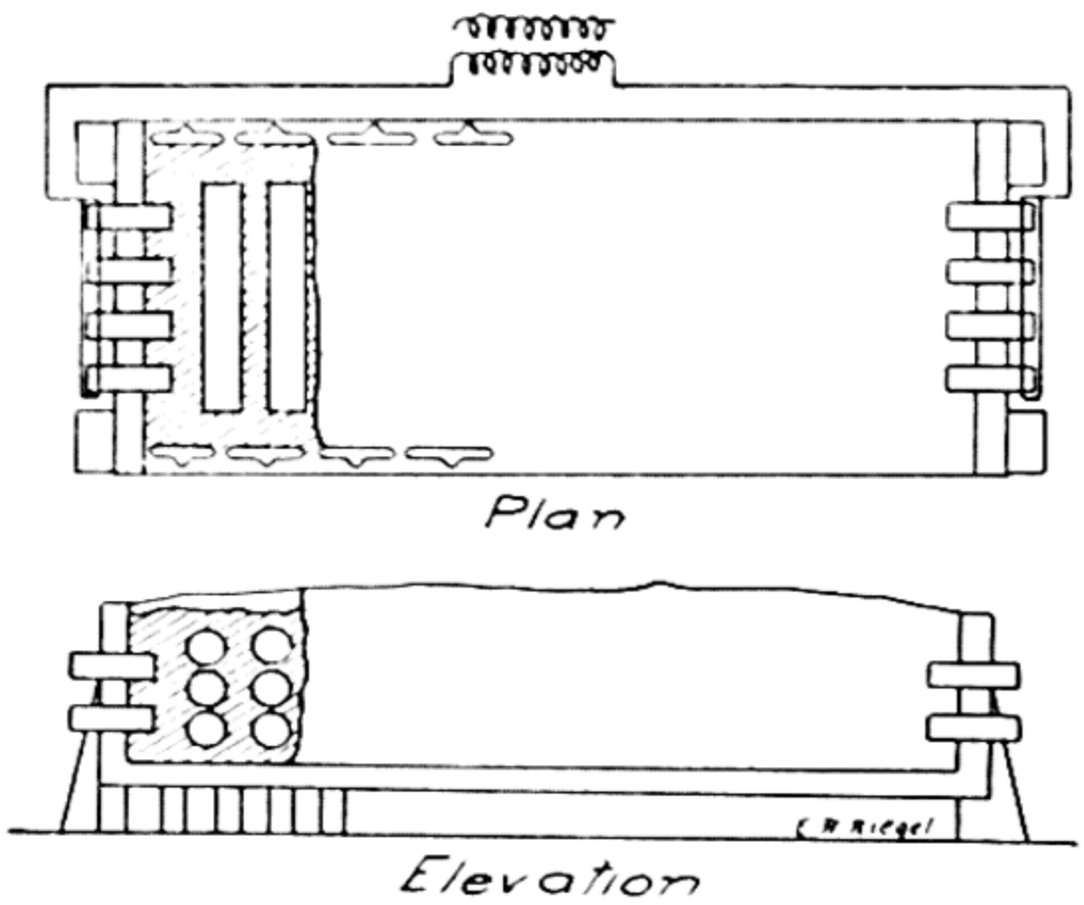


FIGURE 136.—Plan and elevation of artificial graphite furnace for electrodes.

becomes more conductive, and the voltage may be dropped gradually; at the end it is 30 volts. The electrical load is 1600 kilowatts at the start; at the end, 1200 kilowatts; the latter load is in the form of 40,000 amperes at 30 volts. The current from the hydroelectric power plants is delivered as 12,000-volt current and transformed to the lower voltage in oil transformers; it is brought to the graphite block terminals by means of eight copper bars 4 inches wide and three-eighths inch thick.

As the heating progresses gas escapes from the charge and burns. Pyrometers are used for the first few days; then they are removed, as they themselves would be volatilized. The final graphitizing current is on the furnace for two or three days. After the current is shut off, the furnace is allowed to cool for six days (for the largest pieces); it is then unloaded. The complete cycle from one unloading to the next is one month for each furnace. The power consumption is 2.2 kilowatt-hours per pound of graphite. In 1947, a figure of 12.5 cents per pound of graphite electrode was current.

Graphite electrodes may be machined (threaded, for instance) so that when worn short, the butt ends may be screwed onto the next new piece and thus utilized. Electrodes of all kinds are made, of square and rectangular cross-section as well as circular.

The *Söderberg electrode* is a continuous electrode for use in fused electro-

[4] 25 cycles per second.

lytes; it is continuously formed and baked above the furnace, and lowered at the proper rate so as to make the same contact. It consists of a metal cylinder or other metal shape suspended above the furnace with numerous perforations to allow gases to escape; a mixture similar to that for other electrodes already discussed is fed in batches to the cylinder. The heat of the furnace bakes the electrode as it approaches the hot zone. Cylinder and electrode are consumed as the electrolysis progresses; a new section is welded on top of the cylinder as becomes necessary. The electrical contacts slip up the outer casing as the unit is lowered, so that current is fed in at all times. The Söderberg electrode makes continuous operation possible, lowers the cost of electrodes, and permits the use of enclosed furnaces.

The electrode has been applied to aluminum electrolytic furnaces with the mantle made of aluminum. The gases from the closed furnace are washed in an alkaline solution, and a good portion of the fluoride which escapes from the cell is recovered. The Söderberg electrode has been applied successfully to the Hall process for refining bauxite, and to other types of furnace.

Graphite powder is made by filling the furnace with coarsely powdered coke with a central core of 2-inch square graphite rodding, then proceeding as before. Such "bulk graphite" is powdered in a special mill and finds application in the electroplating industry, in dry batteries or cells,[5] and in lubrication. Mixed with grease it becomes a special lubricant.

Certain articles, for example, electric motor brushes, are baked only a short time, and are semi-graphitized.

Artificial graphite is artificial only in the sense that it is manufactured and not found in nature; it is purer and more uniform than the natural material. Its higher purity makes it a better conductor and a superior lubricator. For all uses except the manufacture of clay-graphite crucibles, manufactured graphite excels natural.

"Karbate"[6] is an improved graphite (also carbon) shape which gives improved service in chemical engineering equipment. It is made by forming a synthetic resin *in situ* in the graphite tube, rod or slab, so that the porosity is reduced to zero. "Karbate" is chemically resistant, has good heat transfer, and is twice as strong as the corresponding graphite (or carbon) piece; it has been made into nozzles for steam air ejectors in special services.

Abrasives

Silicon Carbide. In the same kind of electric furnace in which graphite, the softest solid known, is produced, silicon carbide, practically as hard as diamond (the hardest substance known) is also produced; but whereas in the graphite furnace the heat-producing resistance is that of the charge itself, in the silicon carbide furnace a central core of carbon furnishes the needed resistance, and the materials which are to be transformed are heaped

[5] A dry cell consists of a central "raw" carbon rod surrounded by a mix of graphite and manganese dioxide as depolarizers; these are contained in a paper bag, which sets in a mix of starch paste, ammonium chloride, and zinc chloride, surrounded by a zinc cylinder which forms the second pole; the carbon rod is the positive pole.

[6] *Trans. Am. Inst. Chem. Eng.*, 35, 489 (1939).

around it. Hence the silicon carbide furnace belongs to the class of resistance furnaces with indirect heating. It is important to note that the temperature of the graphite furnace is much higher than the decomposition temperature of silicon carbide, so that none of the hard substance can exist in the soft graphite.

Silicon carbide, or silicide of carbon, SiC, was unknown before the development of the electric furnace.[7] Its great value lies in its hardness, and in its property of breaking off to form fresh sharp surfaces. These two properties have led to its use as an abrasive. It is used in the form of grinding wheels, grinding powders, and polishing papers. Silicon carbide is sold under the trade marks of "Carborundum," "Crystolon," and others.

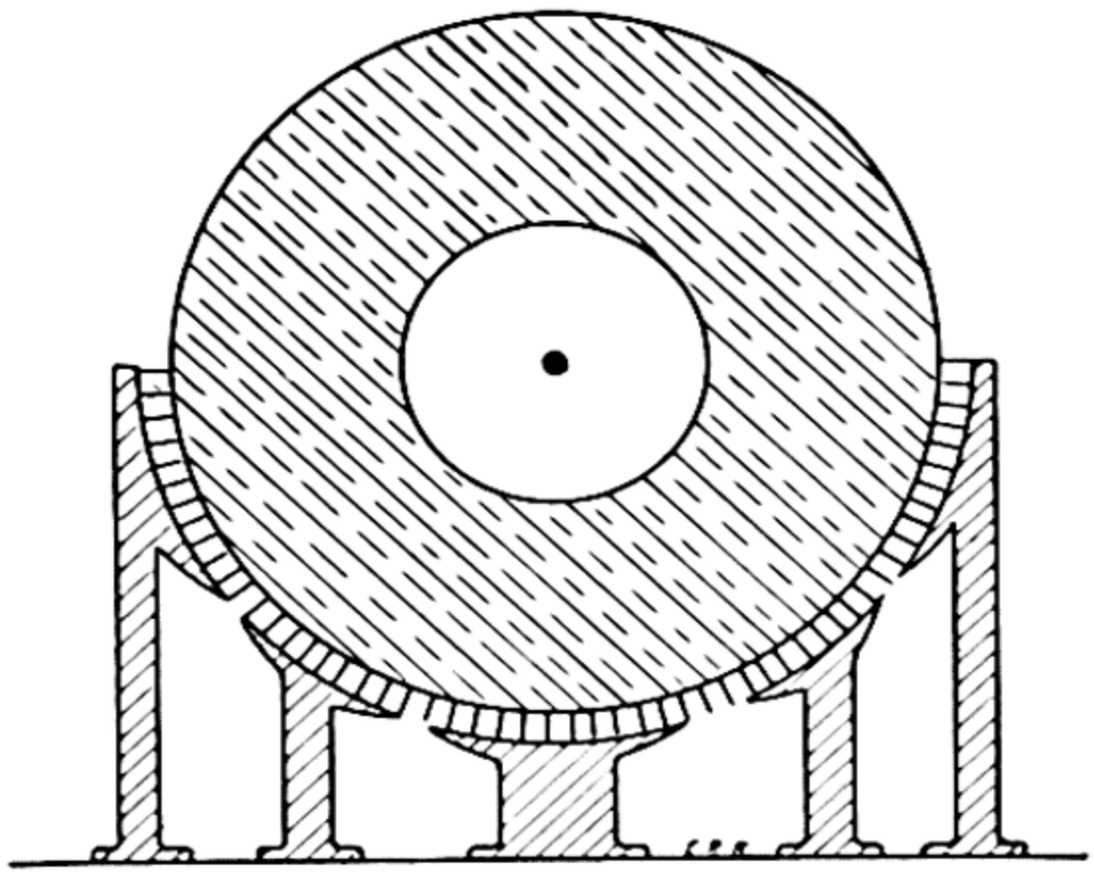


FIGURE 137.—Cross-section of the silicon carbide furnace, showing the central graphite rod surrounded by the core of coke (in blank) and around this the mixed materials forming the charge proper.

Silicon carbide is made in furnaces 40 feet long, 7 feet wide and 6 feet high. The charge itself and the heating core form the greater part of the furnace; the permanent portion is only the bed and the two upright end walls in which the electrodes are imbedded. The bed of the furnace consists of curved cast-iron pieces lined with hard firebrick, on which the charge rests. The materials for the charge are made up in the proportions of 100 parts of the finest grade glass sand, 60 parts of coke, and 10 parts of sawdust (all by weight). These ingredients are thoroughly mixed and loaded from a bucket carried on an overhead crane; the bucket is filled from a bin on an upper floor, by gravity.

The manner of loading the furnace is as follows: Enough material is charged to reach half-way of the height of the total load; a long furrow 2 to 3 feet wide running from one end wall to the other is then made in the center of the charge, filled with crushed coke, and a 2-inch graphite rod [8] extending the entire length of the furnace is laid in the middle. The core widens at the end walls so that all the graphite terminals are in contact with the coke, which then runs without a break to the opposite wall. Next, enough coke is added to complete the core, and then the remainder of the mixed charge. The furnace is then ready for the current. A portion of the charge remains unchanged and forms the blanket required to keep out the air and to conserve the heat.

[7] The experimental work was done at Monongahela City, Pa., by E. C. Acheson.
[8] Made in the same way and from the same mass as the graphite electrodes.

The electrical load is 1500 kilowatts, and is continued until a total of 54,000 kilowatt hours has been applied. The current is alternating (25 cycles at Niagara Falls); the voltage is 300 volts at first, 200 volts at the end. The period of heating is about 36 hours, and the maximum temperature 2600° C. (4624° F.) in the reacting mass.[9] Blue flames are visible all over the mass for the greater part of the heating; they consist of carbon monoxide, escaping and burning. Toward the end these flames turn yellow, as the sodium compounds begin to volatilize and pass out. The furnace is

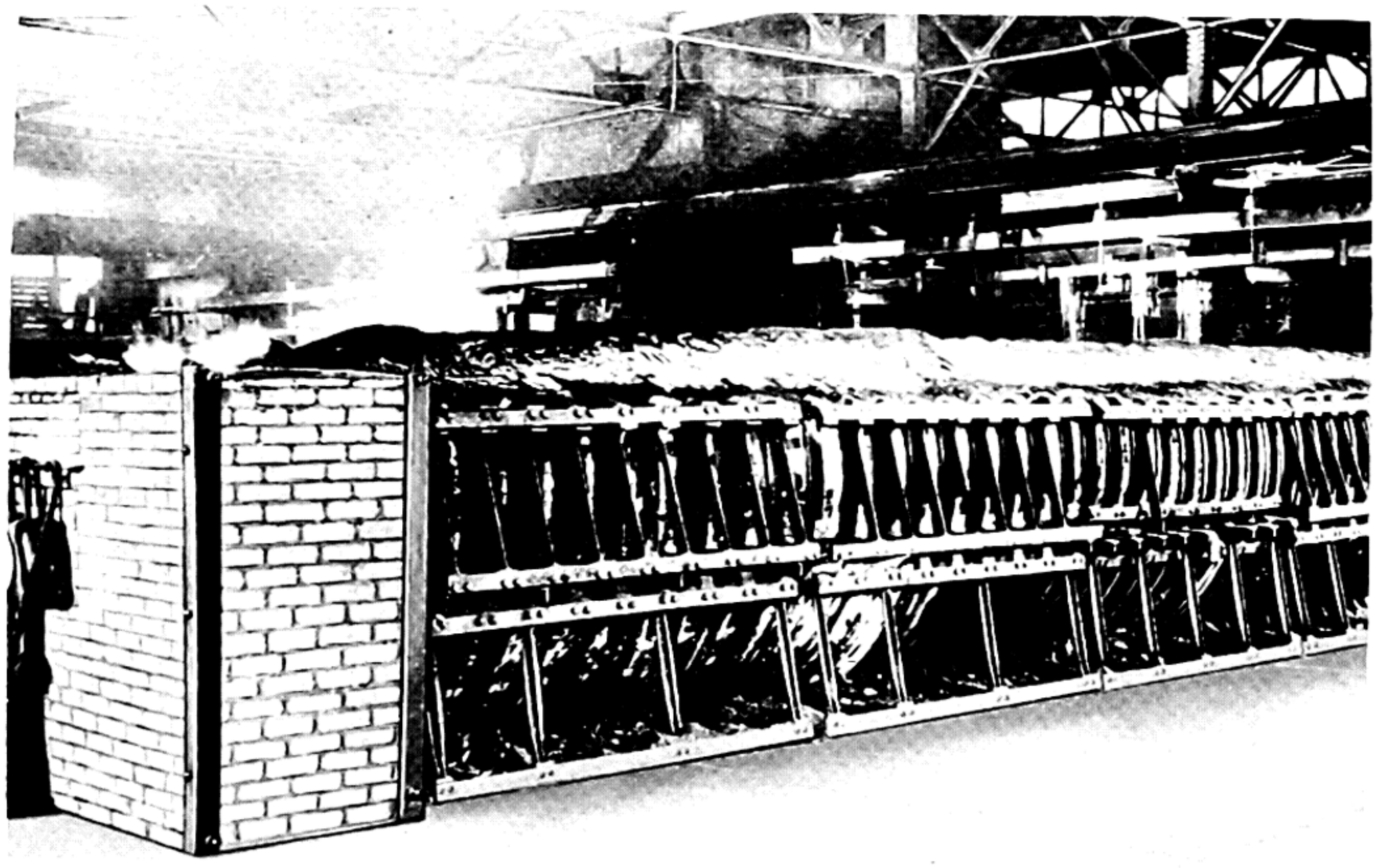


FIGURE 138.—The "Carborundum" brand silicon carbide furnace, an electric furnace with indirect resistance. As shown, the heating period is over, the charge has shrunk from its original volume. The furnace is about to be discharged. (*Courtesy of Carborundum Company, Niagara Falls, N. Y.*)

allowed to cool and is then opened. The inner part of the mixed charge is found to have been transformed into large hard chunks consisting of glistening, well-formed, flat crystals of various colors; some regions have a soft velvety violet color, others are green-bronze to light green, others again are colorless. The color cannot be foretold or regulated; for the manufacturer this is of no importance and perhaps of no interest, but to the visitor a newly opened furnace is a beautiful sight. The crystals are hard, with sharp edges, forming jagged peaks which jut out from the mass.

The desired product forms the inner part of the mixed charge, adjacent to the carbon core, so that moving from the edge inward, there is met first unchanged charge, then the silicon carbide crystal layer; next some graphite having the shape of the silicide crystals, because the crystals first formed have lost their silicon by overheat; finally the inner core, now partly graphite.

[9] "Temperature measurements in commercial silicon carbide furnaces," by Raymond R. Ridgway, *Trans. Electrochem. Soc.*, **61**, 217 (1932).

From 64,000 pounds of mixed charge, about 16,000 pounds of silicon carbide crystals are obtained. The graphite in the center is a by-product; most of it is sold to electrode makers. The cycle from unloading to unloading is one week.

The function of the sawdust is to make the mass porous so that gases may pass out. It will be noted that enough coke is added to remove the oxygen from the sand in addition to the amount required to form the silicide. The reaction is $SiO_2 + 3C \rightarrow 2CO + SiC$.

Silicon Carbide Products. The chunks removed from the furnace are in part stored in the yard, in heaps which again form a striking sight, especially on a sunny day. When needed, the chunks are crushed either in steel edgerunners, the pans of which revolve while the corrugated steel wheels are stationary, or in a train of crushers and crushing rolls, as described later

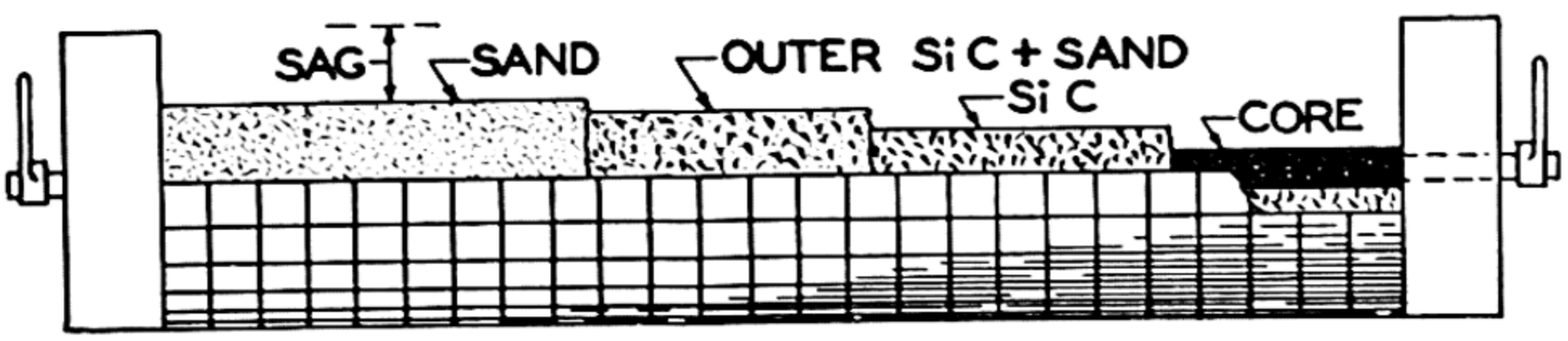


FIGURE 138a.—The charge in the silicon carbide electric furnace, illustrating the several layers in the charge, and the sag after burning.

for fused aluminum oxide. The crushed crystals pass through washers; they are then dried, and sieved on multi-level vibrating screens. Crystals passing a 24-mesh sieve would still be coarse grit, while crystals passing a 120- or 150-mesh sieve would be fine grit. A medium grit might be 54-mesh.

Grinding wheels are the most important silicon carbide product, and are described later. Grinding compounds for automobile valves, for example, are silicon carbide fines, in two sizes, set in a calcium soap jelly. Cloth and paper coated with abrasive crystals, silicon carbide or aluminum oxide are extremely efficient and have displaced to a considerable extent the older emery cloth and sand papers. Abrasive cloth is made by raining a stream of crystals onto a moving sheet of cloth coated with an adhesive. Honing stones, rods and sharpening tools find a ready market.

The high resistance of silicon carbide products to heat has made them useful as super-refractories in many shapes and forms, *e.g.*, slabs (batts, pushers), kiln furniture, end posts, shelves, plate setters and numerous other setters. Such shapes and forms are in great demand because ceramic ware of all kinds is fired increasingly in tunnel kilns, and each car is fitted with shelves carried by end posts, all of which must remain uninfluenced by the high and long heat of the kiln. The setters carry the identical shapes in ceramics without distortion while the firing takes place.

Silicon carbide mixed with 25 per cent of graphite is made into massive crucibles (carbon bond) with walls from $1\frac{1}{2}''$ to $2\frac{1}{2}''$ thick, which serve for melting aluminum and other non-ferrous alloys, *e.g.*, the Tercod crucible,

which may be made by the "spinning" process for high wall density, or by the "jolting" process for high bottom density.

Silicon carbide resistor rods such as Globar serve as heating elements in high-temperature electric furnaces and kilns.

In 1946, about 43 per cent of the silicon carbide production was devoted to non-abrasive uses, while only 3 per cent of the aluminum oxide was so consumed.

Electro-orientation.[10] In the manufacture of so-called sand paper, which may be coated with sand, silicon carbide, or some other artificial abrasive, the deposition of the abrasive grains onto the paper or cloth backing is done under the influence of electrostatic charges, with the result that all the grains adhere to their backings with their sharpest point uppermost. Further, the grains are more evenly spaced. The joint result of these improvements is to give the abrasive paper about 35 per cent increased cutting quality. In the course of application to the backing material, the particles are charged with high-voltage electricity, and move from one electrode to the other, rotating, so that their lines of longer dimensions are parallel to the direction of force; as a result they strike the adhesive in the position desired, *i.e.*, with sharp edges up. Particles so charged repel one another equally, and this leads to equal spacing. The potential applied is 100,000 volts.[11]

It might be remarked in passing that coarse sand paper has 12,000 grains per square inch, whereas fine sand paper has up to 35 million.

Fused Aluminum Oxide. Another artificial abrasive which is made with the help of the electric furnace is artificial emery, a crystalline alumina (Al_2O_3), known in the trade under the names of "Alundum" and "Alox-ite."[12] The naturally occurring crystalline alumina is corundum, which may be transparent and blue (sapphire) or red (ruby); when less pure and colored brown or black, it is emery. The hardness of emery varies; depending on the specimen, it lies between 7 and 9 on the Mohs scale, on which diamond is 10.

The hardness of fused and crystallized aluminum oxide produced in the electric furnace is uniform; its value is 9, just under that of silicon carbide. More aluminum oxide abrasives are manufactured and consumed than silicon carbide abrasives.

TABLE 50.—*Crude Artificial Abrasives Sold, Shipped and Used from Manufacturing Plants in U. S. and Canada (1946).**

Silicon carbide abrasives, crude	63,849 tons;	Value $85.6/ton
Aluminum oxide abrasives, crude	132,084 tons;	Value 63.3/ton

* Minerals Yearbook.

The artificial emery contains about 95 per cent alumina; its color varies from white to yellow to brown.

Fused aluminum oxide is made from bauxite, a hydrated alumina which contains iron oxide in amounts varying from 1 to 20 per cent; it also contains

[10] A branch of Applied Electrokinetics.

[11] "Electrocoating sand paper—a method for procuring increased abrasiveness," *The Electrical Review, London,* 118, 121 (1936).

[12] Also diamantin, electrit, lionite, exolon.

some silica and other impurities (titanium). The bauxite is first calcined, then mixed with fine coke and iron borings in amounts depending on the silica present, and subjected to the heat of a combined arc and resistance furnace. The charge of 21,000 pounds may consist, for example, of 73 per cent bauxite, 5 per cent fines, 3 per cent coke, and 2 per cent iron; the bauxite is (here) 78 per cent pure. The furnace is circular, 7 or 8 feet in diameter at the top and somewhat less at the bottom, and is 5 feet deep.

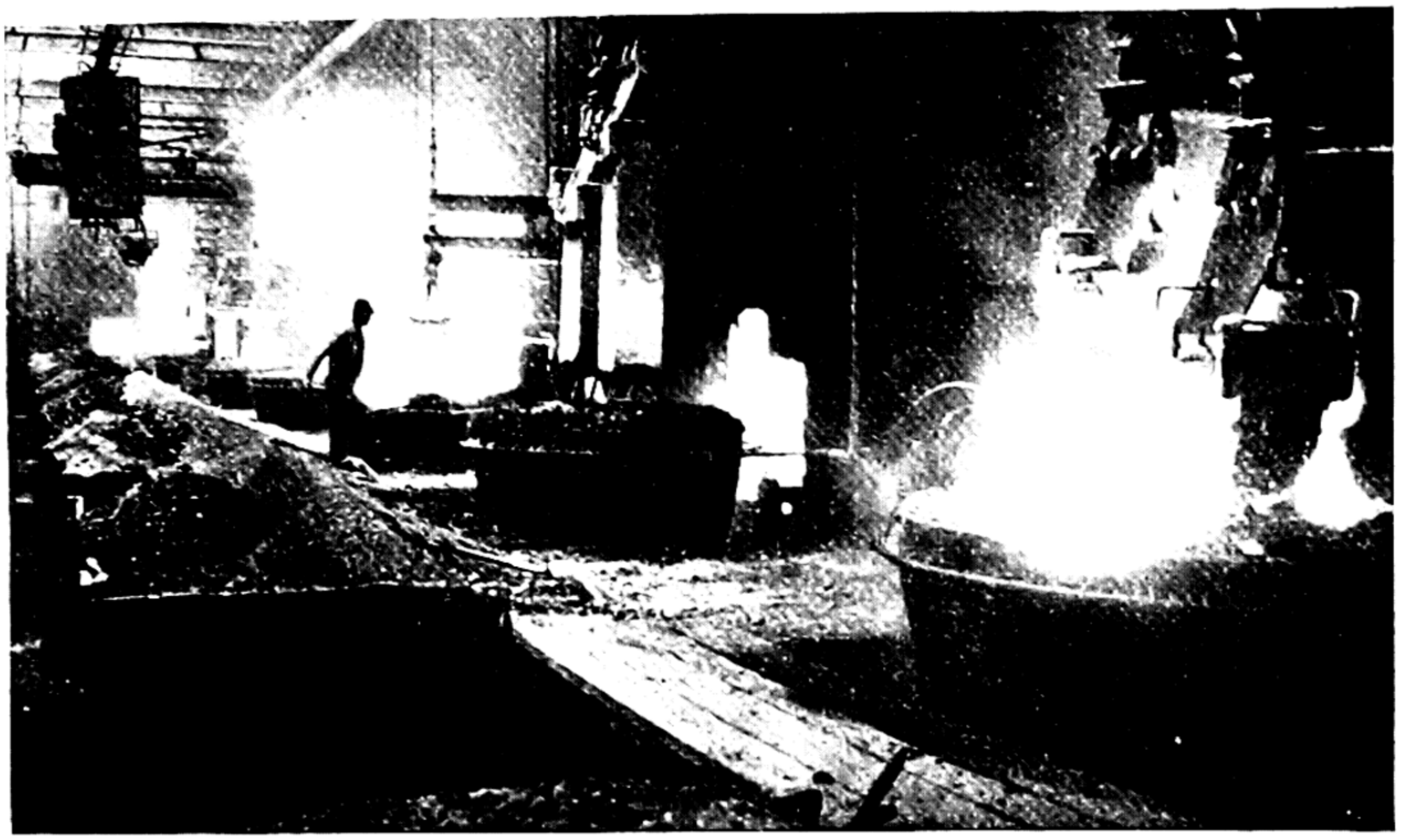


FIGURE 139.—A battery of eight arc-type furnaces in which aluminum oxide abrasive is produced. Aloxite brand aluminum oxide furnaces. (Courtesy of the Carborundum Company, Niagara Falls, N. Y.)

It consists of an unlined steel shell fitted with a carbon bottom or hearth; the shell is water-cooled (spray) while in operation, so that a part of the mass is chilled, forming a protective lining. Two carbon electrodes [8″×8″] of opposite polarity are suspended in the furnace; the current arcs from one electrode to the mass, passes through the mass and arcs back to the other electrode. Increasingly larger amounts of the charge fuse. The electrodes are hung from a cable wound on a drum, and constantly able to move up or down, a correcting action which keeps the current through the furnace constant. When the electrodes dip into the melt, more current passes; the greater current actuates a motor which winds the cable in the direction which raises it. When the electrodes are too far above the melt, the current is too low; the opposite correction takes place, and the cable lowers the electrodes. As the latter wear, the cable lowers them by lowering their supports. During the smelting process, more charge is added gradually until the furnace is filled with melt. To a certain extent, a separation has taken place; the metallic impurities (ferro-silicon) settle to the bottom, the fused

alumina floats on top. The furnace is now cooled, turned upside down, stripped of its shell, and the ingot lifted by a crane and set on the crushing floor. The current applied is 130 volts, 500 kilowatts, and the time for the fusion is 36 hours. The ingot is allowed to cool and is then reduced in size to grains and fine crystals in the operations which follow.

A steel ball dropped on the ingot reduces it to large fragments which are sorted, the proper ones are then fed to a train of crushing devices consisting, for example, of a jaw crusher, a gyratory, and a second gyratory delivering pea size product to 1, 2 or 3-roll crushers. A magnetic pulley on one of the many belts (rubber) removes tramp iron. The fine grains pass through a Canary crusher,[13] which breaks off and removes the fine projections on the grains. Inclined vibrating screens deliver the several sizes (24, 36, 46, 80-mesh, and others.) In one plant, a washer is provided by means of which the exceedingly fine powder, or flour, may be floated off, and later recovered. The grits are ready for the next step, making the grinding wheels.

Grinding Wheels. In making grinding wheels, the manufacturer has a number of factors under his control, which he can vary in order to produce a wheel exactly suited to the task for which it is intended. Among these factors are: type of abrasive, size of grit and mixture of sizes, grade of hardness, density of structure (dense or open), and type of bond.

Grinding wheels are made almost exclusively of artificial abrasives. Silicon carbide is selected for grinding materials of low tensile strength, such as brass, aluminum alloys, copper, and marble. Aluminum oxide is best adapted for grinding materials of high tensile strength, as high carbon steel, alloy steels, and others. The hardness of the final wheel in any one category depends mainly upon the amount of bond; the more bond material in relation to the grits, the harder the wheel. Coarse grits cut rapidly; fine grits cut more slowly, but produce a smoother finish. Wheels made by the puddled wheel process are less dense than those made by the pressed-wheel process; in the latter, the higher the pressure, the denser the wheel. The various bonds are: (1) the ceramic bond, resulting in a vitrified wheel, and (2) silicate, shellac, rubber and resinoid bonds.

For the ceramic bond, grits, water, clay and additions are mixed and pressed into shape (mold) on a hydraulic press (in the pressed-wheel process), dried, and the dried wheel fired either in a periodic kiln, like ceramic ware (see Chapter 10), or to an increasing extent in tunnel kilns. Three-quarters of all grinding wheels have the ceramic bond.

Resin-bonded wheels are stronger, more resilient, and more resistant to thermal shock than ceramic-bonded ones. They are made as follows: the grit is mixed with the granular resin, phenolformaldehyde type, for example, with the aid of a plasticizer. The mix is pressed into shape under a pressure of 1 ton per square inch. Wheels as large as 42 inches are produced. Cut-off wheels, to take a further example, a wheel $\frac{1}{8}$ in. thick, 16 in. diameter, weighing 1200 grams, can be molded in 75 seconds, and are then baked (in saggers) at 400° F. (204° C.) for 40 hours in electrically heated ovens. Resin-bonded wheels are essentially standard for snagging wheels, and

[13] James D. Canary, 3501 Wazee St., Denver, Colorado.

resinoid wheels have proved superior in the grinding of cemented carbide cutting tools.

In general, silicon carbide wheels are black or dark gray-green, while aluminum oxide wheels are brown or purplish brown.

TABLE 51.—*Total Net Grinding Wheel Sales (1947).*

U. S. production	
for domestic use	$79,923,676
for export	4,106,054
Canadian production	
domestic and export	3,722,830
Total	$87,752,560

A pure white and chemically pure alumina crystallized in the electric furnace is also made, in fact to the extent of 10 per cent of the total crystallized alumina production. It is made from pure alumina (purified by the Bayer process, see Chapter 18) with no addition of carbon, and with graphite electrodes in the furnace. Wheels made from this white alumina grind cooler.

In 1946, 12,853 short tons of the white high-purity fused alumina were produced in the United States and Canada, valued at $1,412,950 ("Minerals Yearbook").

Boron carbide. Boron carbide, a comparative newcomer, is made by heating boron oxide with carbon in an electric furnace[14] to a temperature of 2400° C. (4352° F.); the product is harder than tungsten carbide,

$$2B_2O_3+7C \rightarrow B_4C+6CO$$

silicon carbide, and crystallized alumina. On the scale of hardness on which diamond is 15, boron carbide is 14, silicon carbide 13, and aluminum oxide 12 (Norton). Boron carbide is black, and has a glass-like fracture. In powder or grain form, it serves as an abrasive for special purposes; its main use at the present time is in its molded form. When heated to a high temperature under a high pressure, the powder forms a block, with the shape of the mold; the boron carbide liquefies enough to be self-bonding. The nozzles for sand-blasting equipment can be made of this molded boron carbide to advantage.[15]

CALCIUM CARBIDE

To the development of the electric furnace is due another substance not previously known, namely, calcium carbide. It is formed when a mixture of lime and coke is heated to a temperature of 2000° C. (3632° F.) or higher. Calcium carbide, CaC_2, is important chiefly because with water it forms acetylene, used for lighting and for steel-cutting and welding torches; in addition it forms the starting point for one of the several methods of fixing atmospheric nitrogen (cyanamid).[16] It was in this latter

[14] U. S. Patent 1,897,214, to Raymond R. Ridgway.

[15] Trade names for boron carbide are Norbide, Borolon, and others. See "Only a diamond is harder," *Compressed Air Mag.*, 50, 192 (July, 1945).

[16] Chapter 6.

respect that it became of paramount interest to the public in the war emergency of 1918; a plant was constructed at Muscle Shoals, Alabama, which contained very large furnaces.[17] The carbide furnaces fall into the class of combined resistance and direct-arc heating, that is, some of the heat is due to the resistance of the raw materials and product to the passage of the current, but most of it is due to sparking across the charge.

A modern carbide furnace is shown in Figure 140; the long dimension may be 30 feet or more. The charge is 60 per cent lime, CaO, and 40 per cent

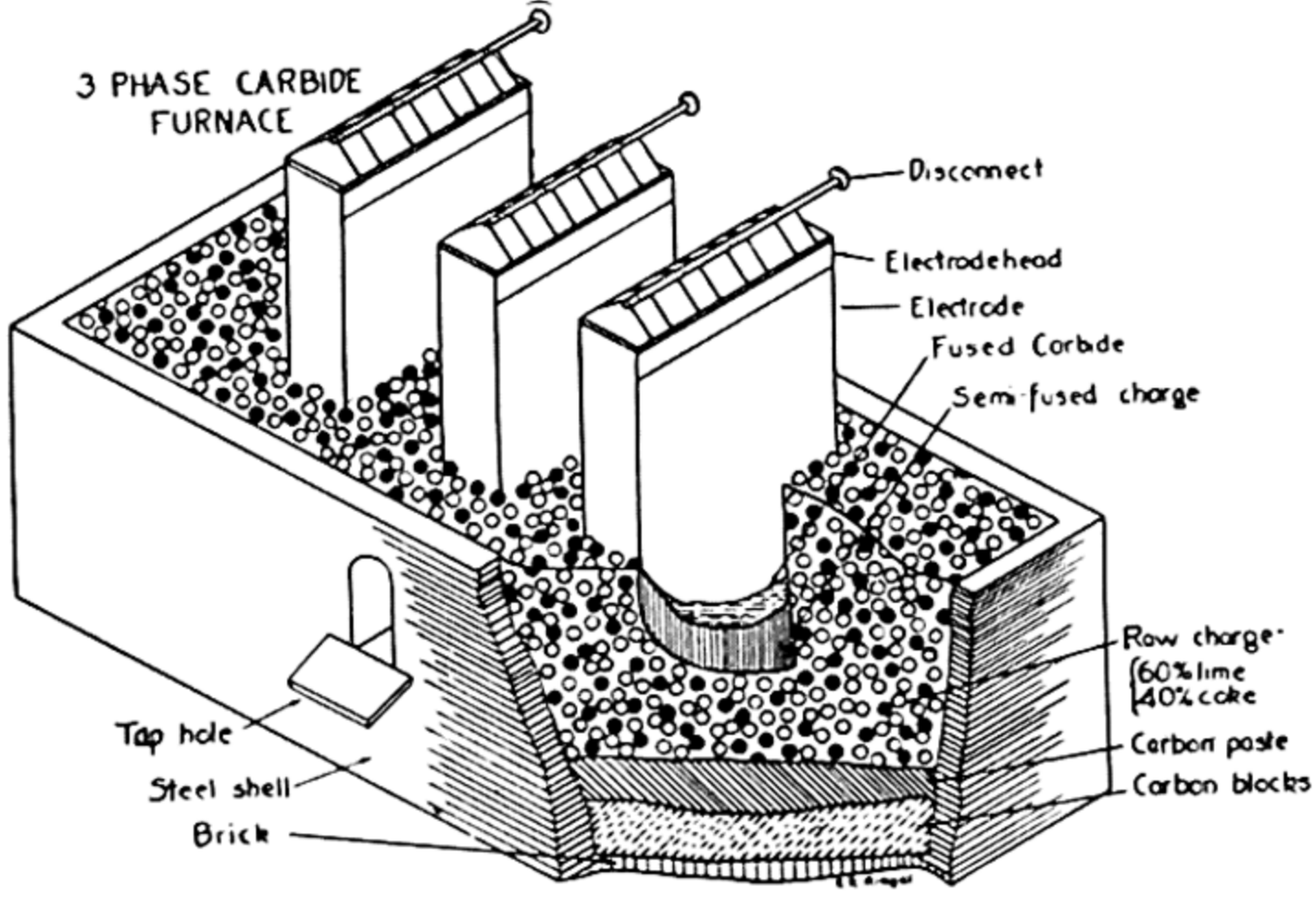


FIGURE 140.—A carbide furnace, with three electrically connected electrodes, and an idle or bottom electrode. The product is tapped and the operation is continuous. (Basic sketch due to the courtesy of the American Cyanamid Co., New York.)

coke. The current is applied through three suspended graphite electrodes, which are adjustable; an idle electrode is formed by the layer of carbon over the bottom. The reaction is

$$CaO + 3C \rightarrow CaC_2 + CO;$$

the carbon monoxide evolved was once wasted, but is now frequently saved for synthetic reactions. The calcium carbide is produced in the form of a melt, and is tapped continuously. No refractory except carbon will withstand molten carbide. It is customary, therefore, to build the furnaces very large, and to depend upon a thick layer of semi-fused material for the actual working lining. In consequence, the active part of the furnace is a small zone immediately surrounding the electrodes; the active charge is only a very few tons.

The raw materials, limestone and coke or coal, must be carefully selected, particularly if the carbide is to be used for acetylene production. The limestone should contain practically no phosphates, for these form phosphides later which on burning leave a white deposit; it must be free from magnesium carbonate, for magnesium does not form a carbide and the presence of its oxide in the charge causes a waste of current. The coke is

[17] The intention was to make calcium carbide, then calcium cyanamide, then by the action of steam in autoclaves on the cyanamide, ammonia. This latter was then to be oxidized catalytically, and nitric acid made. The acid after concentration to 100 per cent was to be used for the nitration of cellulose for munitions. In peace time, the acid would serve to make sodium and calcium nitrates, which are fertilizer materials. The war ended before the plant could be put in operation. Since then, the method of making ammonia from calcium cyanamide has become obsolete. Muscle Shoals as a power plant is a distinct and separate consideration.

hard coke, washed free of dust, selected further for low ash (3 per cent is very low); anthracite is used in England to some extent. Were no selection made, it might well happen that the carbide would be so viscous, because of impurities, that it would not flow.

The liquid carbide flows into "chill cars" of 1000 pounds capacity; the carbide contracts on cooling, so that it is readily dumped. If it is intended for acetylene production, it passes through a jaw crusher,[18] and then through very slow rolls [18] to give a minimum of dust; the pieces are screened to size, 2-inch pieces for large generating tanks, pea-sized for miners' lamps. For making cyanide, the crushed carbide is sent through a continuous pebble mill, which gives a powder, 80 per cent of which passes a 40-mesh screen; this then is fed to a tube mill [18] (pebbles), which gives "milled carbide," 85 per cent of which passes a 200-mesh screen. To remove the possibility of forming an explosive mixture from acetylene, generated by accidental moisture, with air, the grinding is done in an atmosphere of nitrogen.

The crude carbide is 83 per cent CaC_2, 14 per cent lime (CaO), and 1 per cent carbon; it contains small amounts of silicides, phosphides, and sulfides. It will be evident that the raw materials must be carefully selected, when it is remembered that there is no slag which can be rejected; whatever impurities enter the furnace, and are not volatilized, will appear in the carbide.

The electrodes wear away during operation, and the merits of the several furnaces must include a reasonably low carbon consumption; in the furnace described above, it is 70 pounds per ton of carbide.

An important figure is the number of pounds of carbide produced per kilowatt-hour consumed; from the figures given for this furnace it is 2 kilowatt-hours for 1 pound of crude carbide, or 4.3 kilowatt-hours for 1 kilo of crude carbide; expressed still differently, it is 9.2 pounds of product per horsepower day. The current efficiency is then about 62 per cent.

The production of calcium carbide in 1946 was 570,138 short tons.

Other Products of the Electrothermal Furnace

The ferro-alloys are described in Chapter 48.

Carbon disulfide is a product (but not exclusively) of an electrothermal furnace of shaft-like construction [19]; the materials are charcoal and sulfur. The charcoal is fed from the top, and is swept by the outgoing vapors of the product; the sulfur is fed through channels in the walls to the base of the furnace. The electrodes are placed just above the hearth, and the heat is due to the resistance of the charcoal to the passage of the current; this is therefore a resistance furnace with direct heating. The vapors are condensed by cold water and the liquid redistilled. Furnaces in which fuel heat is applied are also in successful use. Carbon disulfide is flammable at comparatively low temperatures, and, mixed with air in certain proportions, explosive; the furnace operates very smoothly, however. The product is of

[18] Chapter 44.

[19] "The manufacture of carbon bisulfide," by E. R. Taylor, the inventor of the process, *Ind. Eng. Chem.*, 4, 557-9 (1912).

value as a solvent; it is used to make carbon tetrachloride, and in the vulcanization of rubber [20]; but its most important use is in the manufacture of viscose silk or rayon.[21]

An electrothermal furnace has been described which receives sulfur vaporized in a separate lower chamber. The furnace proper or upper chamber has 2 electrodes; the carbon is fed as charcoal with a small amount of broken hard graphite pieces introduced just over the electrodes in order to lower the resistance. The carbon mass is kept at red heat.[22]

Tremendous amounts of carbon disulfide, however, are also made in a thermal furnace, with the retorts heated by the more common fuels. Production by all methods was 299,671,000 pounds. (1946, U. S.)

Other Patents

U. S. Patent 1,859,856, production of silicon carbide by charging a mixture of calcium silicate slag containing 85 per cent combined CaO and SiO_2 and carbonaceous material into an arc type furnace; 1,872,202, on making calcium carbide, by forming briquets of coke, lime, and water, drying and smelting them with additions of lime and coke; 1,705,697, 1,705,717, resistance type furnace; 1,737,566, electric furnace for the production of carbon bisulfide; 1,979,052, electric resistance furnace; 2,005,956, method of making abrasive metal carbides, and apparatus; 1,893,106, method and apparatus for electrically fusing nonconducting materials. Brit. Pat. 563,123, abrasive bodies bonded by synthetic resins; U. S. Pat. 2,378,025, apparatus for coating sheets with abrasive particles; 2,389,462, abrasive products; 2,254,612, rubber-bonded articles.

Problems

1. The charge for a furnace run for making silicon carbide is 32 tons of mixed materials, coke, sand, and sawdust, in the proportions specified in the text. 16,000 pounds of crystals of silicon carbide are obtained. Let the sand be 98 per cent SiO_2. What percentage of the total possible product is the amount actually collected?

2. A calcium carbide furnace produces 48 tons of crude carbide, 85 per cent CaC_2, per day. The current is 130 volts, 60,000 amperes. Find the kilowatt hours for each pound of crude carbide, and for a pound of 100 per cent material. What is the horsepower-day per pound? Use the appendix for conversion figures.

3. What is the yield of carbide in Problem 2 on the basis of the lime used, if the lime is 97 per cent CaO?

4. The heat effect in the formation of calcium carbide is included in the reaction below:

$$CaO + 3C \rightarrow CaC_2 + CO + 108.0 \text{ Calories.}$$

Changing these to kilowatt hours gives a theoretical energy consumption of 1.96 kwhr. per kilo of CaC_2. This is on the basis of 100 per cent current efficiency, and for 100 per cent carbide. It also refers to room temperature, while in practice, the reaction takes place at near 2000° C., necessitating a higher consumption of current for heat production, and making up for heat losses by radiation. At 50 per cent energy efficiency, the figure becomes 3.92 kwhr. per kilo of product. The consumption given in the text is somewhat higher. Check all these figures; 1 kwhr. = 860.5 Calories (1 Calorie = 1 kilogram calorie = 1000 gram calories), which figure should also be checked by the student.

Reading References

"Applied electro-chemistry," Allmand and Ellingham, London, Edward Arnold and Co., 2nd ed., 1924.

[20] Chapter 39.
[21] Chapter 22.
[22] U. S. Patent 1,849,140.

"Electric furnaces," Borchers, translated from the German by Solomon, London and New York, Longmans, Green and Co., 1908.

"The Muscle Shoals nitrate plant, No. 2," Andrew M. Fairlie, *Chem. Met. Eng.*, 20, 8 (1919).

"The manufacture of carbide of calcium," Charles Bingham, New York, D. Van Nostrand Co.; London, Ragget and Co., 1916.

"Temperature measurements in commercial silicon carbide furnaces," Raymond R. Ridgway, *Trans. Electrochem. Soc.*, 61, 217 (1932).

"Electrocoating sandpaper," *The Electrical Review (London)*, 118, 121 (1936).

"There is no sand in sand paper," *Scientific American*, 149, 216 (1933).

"Hardness values for electrochemical products," Raymond R. Ridgway, Archibald Ballard, and Bruce L. Bailey, *Trans. Electrochem. Soc.*, 63, 369 (1933).

"Formation and dissociation of silicon carbide," Otto Ruff, *Trans. Electrochem. Soc.*, 68, 87 (1935).

"The preparation and properties of so-called 'beta-alumina'," Raymond R. Ridgway, A. Albert Klein, Wm. J. O'Leary, *Trans. Electrochem. Soc.*, 70, 71 (1936).

"Aromatics, Gas and Coke from heavy Petroleum Residues," E. L. Hall, *Chem. Met. Eng.*, 48, 100 (1941). "Knowles coke ovens" for making petroleum cokes.

"The Söderberg electrode," by C. H. Noton, *The Industrial Chemist (London)*, p. 115, May, 1941.

In contrast to electrolytic decompositions at room temperature, in water solutions, similar decompositions may be brought about by electric current at high temperatures, in a bath of fused salts; such an electrolytic cell may then well be called an electrolytic furnace. It is by means of such a furnace that all our aluminum is prepared, and it is on aluminum, fabricated into aircraft, that the safety of the nation in part depends. A debt is owed to the pioneering manufacturer who kept the commercial processes going in the days when he had to look about for possible uses for his new metal in order to make sales.

Chapter 18

Products of the Electrolytic Furnace (Aluminum, Magnesium, Sodium) and Products of the Electrolytic Cell Other than Caustic

The decomposition of salt in water solution, resulting in the formation of caustic soda and chlorine, by passing direct current through the cell, is the most familiar instance of electrolytic decomposition.[1] Fused salts, free from water, at temperatures which may be red heat and higher, are similarly decomposed. Attempts to treat fused sodium chloride in that way resulted in failure until the advent of the Downs cell. The electrolysis of fused salt is the modern method of manufacturing sodium metal; its comparatively low price permits the use of metallic sodium in the preparation of a number of materials which could not otherwise be made, including sodium peroxide and sodamide. The electrolytic decomposition of aluminum oxide dissolved in fused cryolite ($AlF_3 \cdot 3NaF$) has been completely successful and constitutes the present method for the manufacture of aluminum metal; a similar process serves for magnesium.

The three processes just given are straightforward decomposition reactions, by direct electric current; another type of reaction is performed in the electrolytic cell, chiefly with hydrous electrolytes, namely, that of oxidation at the anode. Examples are the change of sulfuric to persulfuric acid, of manganates to permanganates; these are presented later in this chapter.[2]

Aluminum

The electrolytic process for the manufacture of aluminum was invented by an American, Charles M. Hall[3]; at about the same time, the French

[1] Chapter 5.

[2] Oxidation may also be considered as a partial loss of electrons on the part of a negatively charged ion, at the anode (the plus pole).

[3] U. S. Patent 400,766 (1889); the Hall process was made more efficient thermally by the use of the Bradley internally heated furnace. References to the famous litigation which grew out of this circumstance will be found in "The Law of Chemical Patents," Edward Thomas, New York, D. Van Nostrand Company, 1927. Involved in the litigation and in the early history of the aluminum industry was the Cowles furnace, in which aluminum alloys were produced by electrothermal effect. It has been said that the original Hall patent would not work as written, and that "if it had not been for the Cowles furnace, or the closely related Bradley furnace, Hall would have failed in his effort to produce aluminum on a commercial scale. The Cowles's family physician, an uncle of Hall, was the one who obtained permission for Hall to work at the Lockport plant where the Cowles furnace and an adequate supply of electricity were available."

inventor Héroult devised essentially the same process. Previously, aluminum had been made by the action of sodium metal on aluminum chloride or sodium aluminum chloride; the cost was high, because sodium at that time was made by reducing sodium hydroxide by means of coal in retorts. The production was small.

The principal mineral from which aluminum is electrolytically extracted is bauxite, the hydrated aluminas, $Al_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot 3H_2O$. The importance of aluminum in national defense makes bauxite, its source, an essential war material. Table 52 gives selected production figures for the war year 1943 when production was at its highest. For more recent years, only part of the figures are available; the total world figure given is partly estimated.

TABLE 52.—*World Production of Bauxite, Selected Items.*[4]

	1943 Metric Tons
British Guiana	1,919,060
Surinam	1,655,147
Hungary	1,000,000
France	916,350
Netherlands Indies	600,000
U.S.S.R.	350,000
Yugoslavia	200,000
Gold Coast	162,685
Unfederated Malay States	140,000
United States	6,332,868
Total, World	14,169,000

		Metric Tons
World total	1944	7,476,500
World total	1945	3,926,000
World total	1946	4,000,000
World total	1947	

TABLE 53.—*Production of Crude Bauxite in the United States in Dried Bauxite Equivalent.*[4]

	1943 Long Tons	1945 Long Tons
Alabama, Georgia, Virginia	196,393	70,960
Arkansas	6,036,490	910,412
Total (U. S.)	6,232,883	981,372
Value, per unit of total	$4.92	$5.75

The bauxite ore is distributed among the various consuming industries as follows: alumina, mainly for aluminum, 71.5 per cent; chemicals, such as alum, 8.9 per cent; abrasives, 16 per cent; oil refining, refractories, and others, 3.6 per cent.[4]

The material electrolyzed in the furnace is aluminum oxide, Al_2O_3, dissolved in cryolite, $AlF_3 \cdot 3NaF$. The latter is obtained from Greenland where extensive deposits occur (Ivigtut), the only commercial deposits in the world. The demand for cryolite has been great enough to permit the manufacture of an artificial cryolite. The aluminum oxide or alumina must be

[4] "Minerals Yearbook."

very pure; it is made from bauxite by various processes, of which the Bayer is the best known. The Bayer purification process involves fine-grinding of the bauxite, followed by digestion with caustic soda solution: the alumina dissolves, the iron oxide and other impurities remain undissolved, as a mud. The suspension is diluted somewhat, filter-pressed or separated in thickeners; the clear filtrate or overflow, containing sodium aluminate, $Na_2Al_2O_4$, is agitated with precipitated alumina from a previous batch, when about 70 per cent of the dissolved alumina precipitates in the form of coarsely crystalline trihydrate, $Al_2O_3 \cdot 3H_2O$. This is in turn filtered or thickened and washed; the solid is next dried, calcined, and is then ready for introduction into the electrolytic furnace. The filtrate or overflow is concentrated and used over again.

The Bayer process is best adapted to rich bauxite ore, containing 55 to 60 per cent alumina, and low in silica (below 7% SiO_2). Other purification processes are the Hall, the Pedersen, and the Haglund.

A lime-soda sinter process for the production of alumina from low-grade bauxites and clays was carried to the pilot plant stage during the war by the Bureau of Mines.[5]

The electrolytic furnace in the Hall aluminum process operates at a temperature of about 950° C. (1742° F.). It partakes of the character of both an electric furnace and an electrolytic cell; the substantial current employed for electrolysis also generates heat by virtue of the resistance of the molten electrolyte and cell; hence the furnace must be classed among the resistance furnaces with direct heating.[6] By means of this heat, the electrolyte is maintained in fluid condition and aluminum is electrolytically deposited by the passage of the current.

The furnace or cell consists of a steel shell, the size depending on the current capacity. The shell is lined with firebrick or other insulation, and this is covered with a baked carbon lining. Steel collector plates attached to the shell and buried in the carbon lining carry the current from the cell. (Figure 141.) The bottom may be slightly inclined so that the molten metal can be run to a tap hole. The fused cryolite is contained in the carbon-lined cell cavity; the anodes, made of hard carbon, are suspended from above and may be lowered as they are consumed. During operation, the bottom is covered by melted aluminum, which forms the cathode; the anodes are lowered to within about 2 inches of the metal. The number of anodes per cell varies between 4 and 12, arranged in single or double row; they vary in cross-section and are between 6 and 12 inches square. The number of cells varies with the size of the plant; they are usually arranged in banks of 24.

Alumina is added to the fused cryolite at certain intervals; the content of dissolved alumina is usually about 2 to 5 per cent. The added alumina does not at once sink to the bottom, as its higher density would suggest, but remains suspended in the cell bath long enough to dissolve, thanks to the agitation of the electrolyte which is provided by escaping gas bubbles and by

[5] "The recovery of soda in the lime-soda sinter process for the production of alumina," James M. Hall and Stanley J. Green, *Trans. Am. Inst. Chem. Eng.*, 41, 483 (1945).

[6] Chapter 17.

the effect of the electromagnetic field produced by the large currents flowing through buses, cell walls and linings. The electrolyte bath is covered with a frozen crust of electrolyte and alumina, so that the surface of the cell presents a white appearance, with no liquid visible. A certain amount of fluorspar, CaF_2, is sometimes added to lower the fusion point of the electrolyte. The

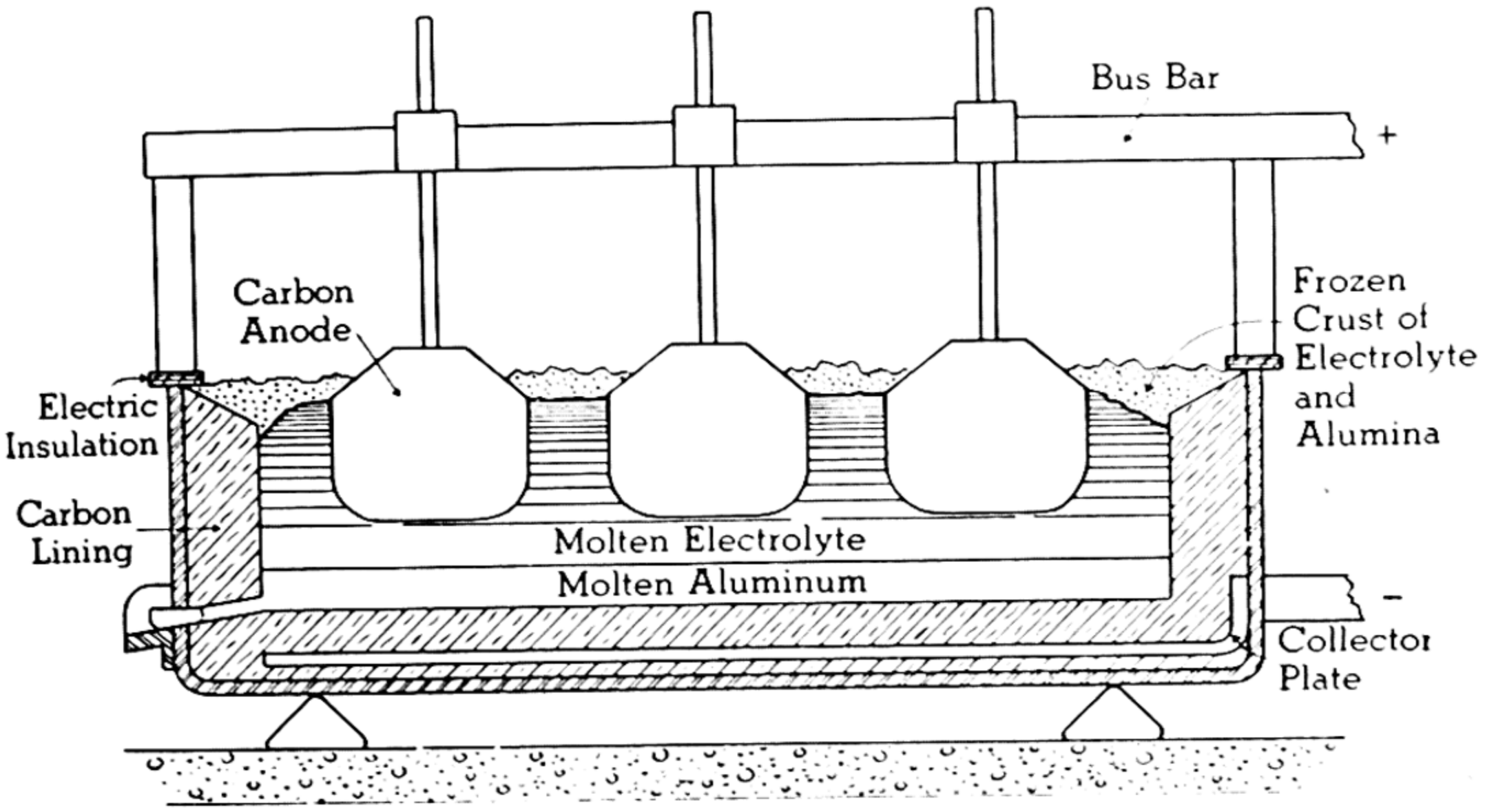


FIGURE 141.—Cross-section of the electrolytic furnace for making aluminum from alumina in a bath of cryolite. The several parts are labeled. (Compare the view in the picture just following.) (Drawn and kindly supplied by the Aluminum Company of America through Mr. Douglas B. Hobbs.)

density of the melted electrolyte must be kept lower than that of the melted aluminum; otherwise the metal does not collect on the bottom.[7] The reaction is primarily:

$$Al_2O_3 \longrightarrow 2Al+3O; \qquad (1)$$

but the oxygen attacks the anode, forming carbon dioxide. Hence the total reaction is:

$$Al_2O_3+1\tfrac{1}{2}C \longrightarrow 2Al+1\tfrac{1}{2}CO_2. \qquad (2)$$

The carbon dioxide forms some carbon monoxide at the hot anode, so that the gas evolved contains some 10 to 50 per cent monoxide. The gases pass out through the cryolite to hoods placed above the cells. The decomposition voltage for alumina at 915° C., dissolved in fused cryolite, and reacting as in (2), is 1.55 (see problem 6). The normal drop in voltage per cell is 6 to 7; a rise indicates that more aluminum is needed. If aluminum becomes dispersed in the cryolite as a metal fog or mist, it may be carried to the anode, there to be oxidized by the atomic oxygen, forming alumina again; the current efficiency [8] is thereby lowered. This happens to some extent at

[7] Molten aluminum at 950° C. has density 2.36; solid aluminum, 2.58; fused cryolite (impure) (950° C.) has a density of 2.17; solid cryolite, 2.9.

[8] Chapter 5.

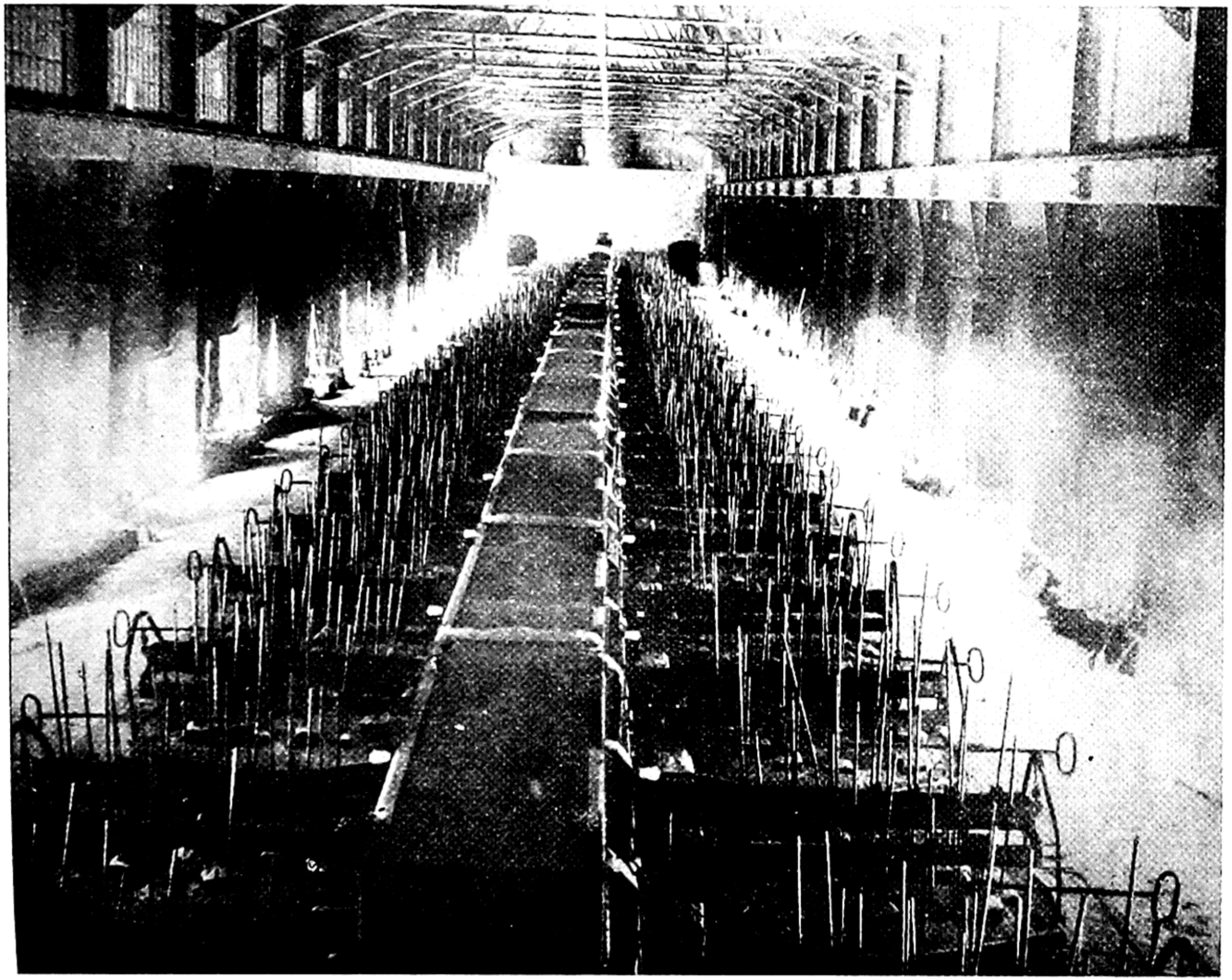


FIGURE 142.—A view of a row of electrolytic cells or furnaces producing aluminum. Note the anodes and anode rods connected to the bus bars, the hoe lying lengthwise on the cell for spreading the fresh alumina. The vessels into which the metal is tapped are set below the floor just in front of each cell, not visible from the central position. (Compare line drawing just preceding.) (Courtesy of the Aluminum Company of America, Pittsburgh, Pa.)

all times, along with other disturbances, so that a current efficiency of 70 per cent is considered good. The amperage varies with the size of the cell. It may be 8,000 amperes for the small ones, and as much as 40,000 amperes for the large ones. Each cell is tapped once a day, giving for the smaller cells about 100 pounds of metal per day. The power requirement in the newer cells is as low as 9.5 kwhr per pound of metal. The anode consumption is 0.6 to 0.7 pound per pound of metal. Two pounds of alumina are consumed to make one pound of metal.

Aluminum is prized for its low density, its resistance to corrosion, its good electrical conductivity, its pleasing color, resembling silver, and the high strength of some of its alloys. These properties have led to numerous uses, such as for the construction of chemical vessels, kitchenware, electrical transmission lines,[9] architectural applications, and in the transportation industry, on land, sea, and in the air. The demand for all available aluminum for the armed services [10] in the war years is now over. The metal is no longer denied to civilians; on the contrary, efforts are being made to find new uses. The high cost of the normal materials of construction for buildings has benefited the metal; sheet aluminum serves for roofs, walls and doors; aluminum clapboards covered on their weather side with a white baked enamel may be seen on almost every city street. Many articles of aluminum are popular because of their lightness, as for example garden tools and tall ladders. In the industrial field, the lighter metal makes possible the construction of massive carbon-crucible molds in sections which now can be carried about by one man. Aluminum-clad steel in the higher gauges has replaced galvanized iron in many new constructions, because the latter could not be obtained (air ducts). Of the chemical uses of aluminum, it may be said that the avidity with which it combines with oxygen at high temperatures has led to its use in deoxidizing Bessemer [11] and open-hearth steel, and in the thermite process.[11]

Commercially pure aluminum is generally considered to contain about 99 per cent of aluminum with minor proportions of iron and silicon which, in reality, act as alloying additions and give the metal greater strength and hardness.

The strength of aluminum is greatly increased by alloying with small percentages of other metals, such as copper, magnesium, manganese, silicon, iron, zinc, nickel, and chromium. Certain alloys can be given additional strength by heat treatment. "Duralumin" is such a "strong alloy"; it contains 4 per cent copper, 0.5 per cent magnesium, 0.5 per cent manganese, and the silicon and iron present in the aluminum as produced in the electrolytic cell. The alloy, in wrought form, is heated to 500° C. (932° F.), quenched, and aged 4 days; the resulting bars have a tensile strength of 60,000 pounds per square inch, equal to that of mild steel. Aluminum and

[9] There are more than a million miles of aluminum cable transmitting electrical current in the U. S. today.

[10] A fighter plane requires about 5500 pounds of aluminum for its construction; a medium bomber contains 13,000 pounds of aluminum, and may contain as much as 1000 pounds of magnesium, as well as 550 pounds of stainless steel and 4000 pounds of alloy steel.

[11] Chapter 48.

its alloys can be fabricated into many commercial forms such as plate, sheet, foil, bar, rod, tubing, wire, extruded shapes, and made into castings by the sand, permanent-mold, and die-casting processes. Aluminum bronze is an alloy of copper with about 10 per cent aluminum.

The method of purification or refining, known as the Hoopes process, illustrates how small differences in properties may form the basis for successful large-scale operation. An electrolytic bath of fused cryolite, to which certain amounts of barium fluoride are added to adjust the density, is employed in this process. A heavy aluminum alloy forms the bottom anode layer in the refining cell. A layer of pure aluminum is light enough to float on the top of the heavier electrolyte, forming the cathode upon which the pure aluminum, electrolytically dissolved from the anode layer, is deposited. The impurities stay in the bath. By this process, aluminum of 99.99 per cent purity is produced. As with many other metals, the properties of this high-purity aluminum are quite different from those of the less pure varieties.[12]

The annual production of aluminum primary metal in the United States climbed steadily from 206,184 tons in 1940 to a high of 920,179 tons (short) in 1943; it then dropped sharply, reaching 409,630 tons in 1946. The installed capacity for aluminum ingot was 883,000 tons, including the War Assets Administration plants, in 1946. The installed capacity for alumina from bauxite is 2,448,000 tons.

Aluminum is quoted at 17 cents a pound (November, 1948), far less than copper (23.5 cents). Besides the industry which produces primary metal, there is an extensive business in remelting scrap, producing secondary metal; 278,073 tons of such metal were produced in 1946.

For the production of one pound of		
aluminum	there are required	10 kilowatt hours
magnesium	there are required	9–10 kilowatt hours
sodium	there are required	7 kilowatt hours

Magnesium

The peace-time demand for magnesium metal since 1946 has been disappointing. The production of primary metal in 1946 in the United States was 5,317 short tons; the world production 13,200 tons. The highest production was in the war year 1943, when 183,584 tons of primary metal were produced (U. S.), and the world production came to 263,000 tons. During 1946, magnesium metal was 20.5 cents a pound.

Magnesium is made (1) by the electrolysis of fused anhydrous magnesium chloride, in a cell whose bath contains potassium chloride; (2) by the electrolysis of magnesium oxide in a bath of fluorides; (3) by the carbothermic process; (4) by the ferro-silicon process (Pidgeon).

Method (1) is the most important, the oldest, and probably the only one now in use (1948). The fusion point of magnesium chloride, 708° C. (1306° F.), is lowered by admixtures of potassium chloride; an equivalent mixture, or anhydrous carnallite ($MgCl_2 \cdot KCl$) melts at 460° C. (860° F.).

[12] Frary, F. C., "Electrolytic refining of aluminum," *Trans. Am. Electrochem. Soc.*, 47, 1 (1925).

Magnesium metal melts at 650° C. (1202° F.). The cell is operated at just above the latter temperature, so that the globules of magnesium which form may rise to the top of the fused chloride. The pot is the cathode, and is connected metallically to a secondary iron cathode, a cylindrical sleeve surrounding the graphite rod in the center of the melt. The graphite rod is the anode. By means of proper construction of the cathode sleeve, a circulation of the melt can be set up which aids the rise of the globules [13]; they reach an annular gutter which faces downward, and is set in the melt near its upper surface. The metal is withdrawn from this after it has cooled to a point where it no longer takes fire when exposed to the air.

The second product of the electrolysis is chlorine; it is handled like the chlorine from the sodium cell, described later. The decomposition voltage for fused magnesium chloride at 700° C. is 3.01; the actual operating voltage is 5 or 6. For the production of 1 pound of metal there are required 4 to 5 pounds of anhydrous magnesium chloride. The current efficiency is 70 to 80 per cent. When the cell is fed with magnesium chloride, all of the latter is withdrawn in the form of metal and chlorine gas; but when the cell is fed with fused carnallite, there is an accumulation of potassium chloride which is unaffected by the current, and a periodic removal of the cell bath is necessary.

The magnesium chloride is obtained in a number of ways: from the mother liquors of brines, the original method in the United States; from carnallite; or from sea water, which contains 0.42 per cent of magnesium chloride. The Dow Chemical Company, which produced magnesium for many years from brines at its Michigan plant, constructed and operated the plant at Freeport, Texas. Sea water is pumped to a flocculator, and milk of lime (made from calcined fossil oyster shells) is added. The magnesium hydroxide suspension is "thickened" mechanically in Dorr thickeners, and then filtered with the aid of Moore filter leaves, which may be lifted out of the tank by a crane and moved above a neutralizing tank. The mud, blown into the tank, is neutralized with 10 per cent hydrochloric acid, the solution concentrated and the salt dried in a huge shelf drier. The still somewhat hydrous product is mixed with flakes of some of the previously dried product and passed through a gas-fired rotary drier, where the drying is completed. The anhydrous product is now ready for the cells. The clear overflow from the Dorr thickeners is discharged into a canal which delivers it to the sea at a point seven miles from the intake, where the sea currents carry it in the opposite direction so that the discharge cannot dilute the incoming sea water. The chlorine from the cells is burned in natural gas and in hydrogen from other electrolytic processes (caustic cells) to form hydrogen chloride, which after absorption in water is the acid used in the neutralizing tanks. A good part of the chlorine is thus recycled. The cells at Freeport are rather large, 6 feet by 12 feet in area, and produce about 1000 pounds of metal each per day.

There is still another way to produce magnesium chloride, and that is

[13] U. S. Pat. 1,851,817.

by chlorinating a mixture of mangesite ($MgCO_3$) or magnesia (MgO) and coke in an electric resistance furnace in the shape of a tower.

Magnesium by method (2), that is, by the electrolysis of magnesium oxide made, for example, by calcining brucite ($MgO \cdot H_2O$) in a cell consisting of the fluorides of sodium, magnesium and barium, is operated at a high temperature, with the cell bath at around 950° C. (1742° F.). Unlike aluminum oxide in cryolite, magnesium oxide dsisolves only to the slightest extent in the molten fluoride electrolyte bath. There is no by-product in this cell process.

In the carbothermic process (3), operated at Permanente, California, pellets of magnesia and petroleum coke are heated to 1900° C. (3452° F.) in an electric reduction furnace. In order to supply the magnesia, dolomite is calcined, and then reacted with sea water, in which the calcium of the dolomite replaces the magnesium; hence half the magnesium comes from the dolomite, half from the sea water. The reaction

$$MgO + C \rightleftarrows Mg + CO$$

takes place. The mixed vapors of magnesium and carbon monoxide must be shock-chilled with natural gas (or hydrogen) to prevent a reversal of the reaction. The magnesium dust formed, carried in the natural gas and carbon monoxide, is cooled further and collected in bag filters; the combustible gases are recovered. The crude dust is compressed into pellets which are fed into sublimation retorts heated electrically to 800° C. (1472° F.). The metal distills in a vacuum, and condenses to crystals against a removable steel liner at the top of the retort. Since the war a continuous method for subliming the metal was developed as far as the pilot plant stage, but the decrease in the demand for magnesium metal and the increased cost of natural gas at the plant site have made it advisable not to resume commercial operation.[14] The production of metal at Permanente over the war period was 19 million pounds; in addition 80 million pounds of Goop, an incendiary containing magnesium powder, were also produced.[15]

Eminently suited for war time production is the Pidgeon process (4) [16] in which ferrosilicon and magnesium oxide or dead-burnt dolomite are made into briquets and heated in closed, evacuated, alloy-steel retorts. The temperature is 1150° C. (2102° F.). Magnesium metal collects in the condenser attached to the top of the retort in solid masses. Each pound of 75 per cent ferrosilicon produces 1 pound of magnesium.

Magnesium is used both as such and in the form of alloys. The magnesium base alloys with 85 per cent and more magnesium serve for making fabricated products (65 per cent). Aluminum alloys and other alloys consume about 30 per cent of the magnesium production. In the war period, the

[14] Private communication from Dr. A. C. Byrnes, Director of Research, The Permanente Metals Corporation, Oakland 12, California.

[15] *Chem. Eng. Progress,* 43, 172 (1947); see also "Production of magnesium by the carbothermic process at Permanente," T. A. Dungan, T. P. 1671, *Metals Technology* (February, 1944).

[16] "Magnesium from dolomite by ferrosilicon reduction," D. H. Killeffer, *Chem. Eng. News,* 20, 369 (1942).

aircraft industry used 80 per cent of the structural magnesium alloy products, mainly in the construction of engines. Magnesium alloys can be cast, rolled, forged and machined.

TABLE 54.—*Typical properties of cast and wrought magnesium alloys.*

Alloy Designation	Nominal Composition* (%)			Tensile Strength	Yield Strength	Elongation (%)
	Aluminum	Zinc	Manganese	(lbs. per sq. in.)		
AM265 as cast	6	3	0.2	27,000	11,000	6
AM265-T4 Cast and Heat-treated	6	3	0.2	37,000	12,000	9
AM260-T6 Cast and Heat-treated	9	2	0.2	38,000	20,000	3
AM3S Sheet (annealed)	..	..	1.5	32,000	17,000	16
AM-C58S Forging	8.5	0.5	0.2	45,000	30,000	6

* Balance magnesium.

Magnesium serves also for flares and incendiary explosives; for flushing radio tubes to remove traces of gases which pumps and charcoal cannot remove. In 1944, 9,080 tons of aluminum powder were produced; in 1946, only 192 tons.

TABLE 55.—*Relative weight of structural metals.*

	Specific gravity	Relative weight	Weight per volume
Magnesium alloys	1.8	1.0	112 lbs./cu. ft.
Aluminum alloys	2.8	1.6	175
Zinc	7.1	3.9	443
Cast iron	7.2	4.0	450
Steel	7.9	4.4	493
Copper	8.9	4.9	556
Lead	11.3	6.3	706

Magnesium salts have been produced from various sources, from bitterns, from brines, and from sea water directly.[17]

SODIUM

Sodium metal was made originally by the electrolysis of fused caustic, the metal being the sole product. Cells holding 250 pounds of melted caustic with a central iron rod as cathode, surrounded by a nickel perforated cylinder as anode, were operated within the range of 315° to 320° C. (599° to 608° F.). The current efficiency was 45 to 55 per cent, the voltage 4.5 to 5.5 per cell. The total reaction in the cell may be written:

$$4NaOH \rightarrow 4Na(cathode) + 2H_2O + O_2(anode).$$

The present method for the manufacture of sodium metal M. P. 97.6° C. (208° F.) is the electrolysis of purified and absolutely dry fused salt NaCl. Sodium made directly from salt is much cheaper than that made from

[17] "Oceans of raw materials for magnesium compounds," by Paul V. Manning, *Chem. Met. Eng.*, 43, 116 (1936).
"Magnesium compounds from ocean water," by H. Henry Chesny, *Ind. Eng. Chem.*, 28, 383 (1936).

caustic, since the latter is itself a manufactured article, whereas salt is found in nature. Besides, a second product, chlorine, is obtained in a high state of purity. The Downs cell,[18] shown in Figure 143, operates on fused salt. The operation is continuous; the sodium produced is collected in a separate compartment, whence it is withdrawn periodically. The chlorine is sent out free from moisture, and is used in gas form, or as a liquid. (See Chapter 5.)

At the carbon anode, 1, the chlorine gas is evolved, and is collected in the dome 3; it passes out under its own pressure. The cathode, 2, is an

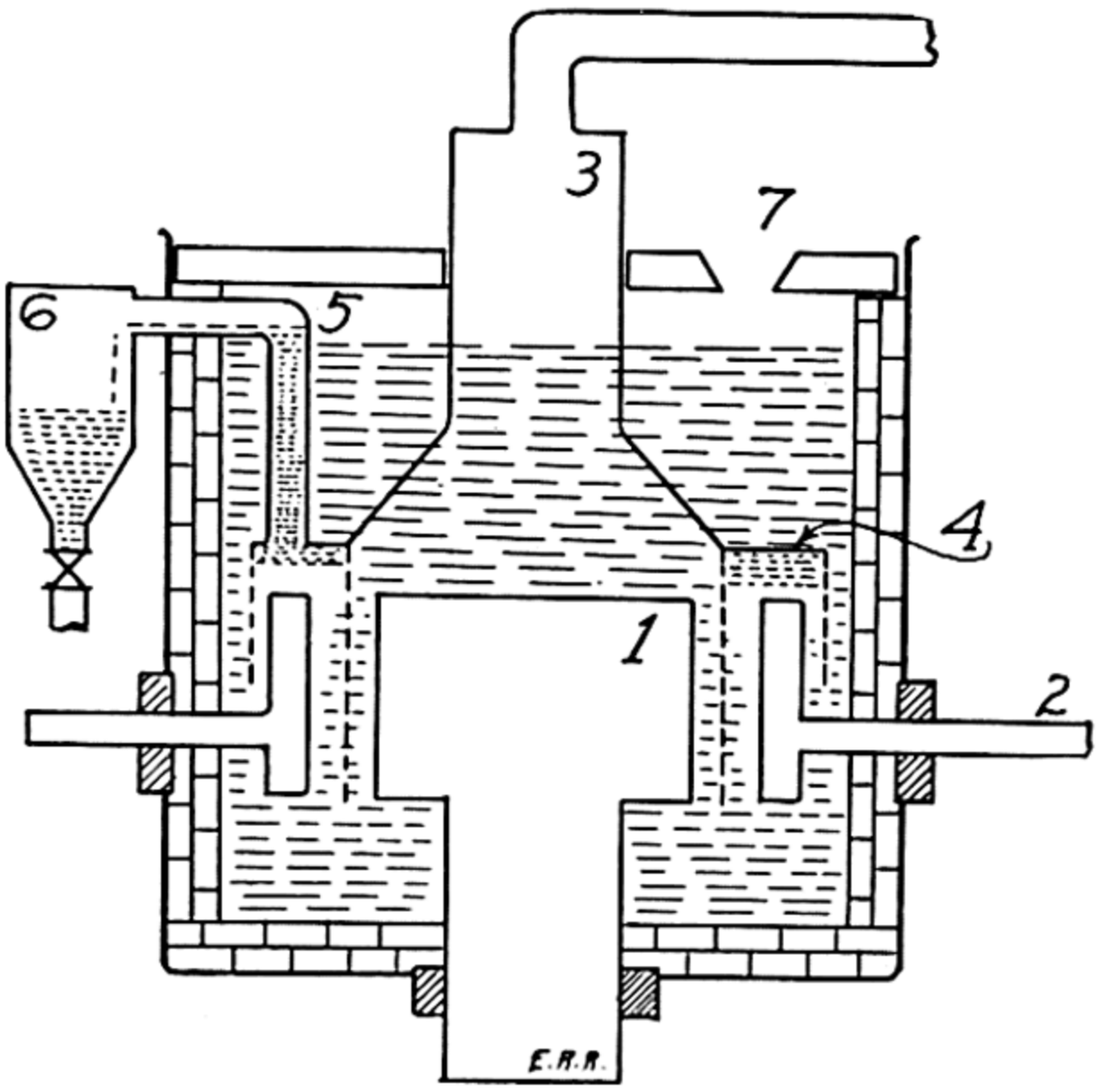


FIGURE 143.—The Downs cell, circular in its horizontal cross-section, producing metallic sodium from fused salt. 1, carbon anode; 2, iron cathode; 3, dome for escaping chlorine; 4, annular sodium collector.

annular iron or copper piece which surrounds the circular anode; the cathode piece has projecting side arms for the electrical connections. A thin but rigid iron screen, cylindrical in shape, is positioned in the free annular space between the anode outer wall and cathode inner surface, yet touching neither one. Its function is to facilitate the collection of the metal. In the sketch, the iron screen is indicated by two dotted lines. The distance between anode and cathode is kept at a minimum, such as $\frac{3}{4}$ inch. The cathode is surmounted by an annular gutter facing downward and set in a plane having a slight angle with the horizontal; the gutter becomes the sodium collector. Sodium metal is generated at the cathode and forms into drops and droplets, both of which rise readily, for melted sodium is lighter than the cell bath. Drops and droplets collect in the sodium collector. The latter is provided with a riser, 5, which delivers the sodium to a closed compartment, 6, from which it is withdrawn at stated intervals. The level of fused salt in the bath is kept high enough to force the column of sodium along the delivery arm of the riser. Fresh salt is introduced at 7, and as it fuses it loses any water it may still contain, which passes out to the room. The housing of the cell consists of glazed refractory shapes set in a steel shell. The anode projects through the bottom of the cell, and is accessible from the floor below for electrical connection. The cathode of one cell is connected metallically

[18] U. S. Pat. 1,501,756 (1924), to J. C. Downs.

and externally to the anode of the next, whose cathode in turn is similarly connected to the anode of the next. A number of cells, in a real sense, furnaces, are set in a row or bank. A powerful flow of air ventilates the cell rooms.

Sodium chloride fuses at 800° C. (1472° F.), but the cell is operated at a lower temperature, such as 600° C. (1112° F.), thanks to the addition of calcium chloride (mainly) to the cell bath, which has the effect of lowering the fusion point. The calcium chloride is unaffected by the current. The lower temperature not only permits a longer life to the cell, but avoids the sodium metal fog which in some of the earlier inventions baffled all efforts to collect the metal produced. A small amount of sodium hydride (a white solid) forms at times and rises to the surface, and causes small explosions. The current efficiency is high, above 80 per cent, and the cells are as large as 20,000, 24,000, and 30,0000 ampere units. In such a cell, the anode may be 35″ in diameter at its upper face, and 4 feet high. The decomposition voltage for fused NaCl at 600° C. is 3.59; operating voltage, 7 to 8.

The liquid metal gathered from the sodium compartments (labeled 6 in the sketch) at the cells is filtered, and is used in further operations in the plant in the form of liquid, or in the form of solidified 12-pound bricks. For shipment, the latter are packed in air-tight steel drums, without any surrounding liquid of any kind. When poured into the forms, the liquid sodium looks just like mercury. Bricks of smaller weight are available. Metal in the liquid form for consumption in the plant is moved in an overhead, insulated and heated (electrical resistor) steel pipe line (2½″), by the application of a partial vacuum; nitrogen gas overlies the sodium in all vessels. Sodium is also shipped to distant points by tank cars of 80,000 pounds capacity, fitted with steel coils on its outside through which cold oil is circulated while loading. With the metal in the solid state, the car is shipped. At its destination, hot oil is circulated through the coils; the sodium is melted and unloaded as a liquid. A nitrogen atmosphere is provided throughout.

Sodium metal is in great demand, for it has many uses, and new ones are being developed constantly. The production is of the order of magnitude of 200 tons per day. Sodium metal is quoted at 16½ cents (1948); it was 20 cents in 1942. The Downs sodium cell is an American invention, and its worth has been established in American plants.

An electrolytic cell furnace at one time reported in successful operation in Germany produced sodium metal.[19] The amalgam from the mercury brine cell may be passed to a second cell, a fused salt electrolytic cell with rotating disk, to produce sodium metal.[20]

Sodium metal is an industrial chemical; it is indispensable in the manufacture of sodamide, sodium cyanide, sodium peroxide, sodium hydride, and as the metal in the reduction of organic esters and other organic reactions; it is the basis for the lead alloy used in the manufacture of tetraethyl lead. Sodium may be used to improve the structure of certain alloys, to purify molten metals, for metal descaling (recently developed), and as a heat-

[19] U. S. Pat. 1,820,844; of interest also are 1,074,988 and 1,092,178.
[20] *Chem. Ind.*, 61, 48 (1948).

transfer agent.[21] It may be made into a chlorine-free sodium hydroxide by adding the metal, with suitable precautions to a concentrated hydrous caustic solution. The properties listed in Table 56 may lead to other applications.

TABLE 56.—*Physical properties of various fluids suitable for transmission of heat including metallic sodium.*

Property	Sodium	Mercury	Tin	Meprolene Oil	Diphenyl $(C_6H_5)_2$	Water
Melting point, °C....	97.5	−38.8	232	0±	69	0
Boiling point						
760 mm.	833° C.	357	2270	300±	255	100
75 mm.	677° C.					
13 mm.	565° C.					
Density, gms./cc.	0.834 (98-883° C.)	12.9 (100-400°)	6.93 (232-400°)	0.91 (20°)	.85 (255°) 1.04 (20°)	0.998 (20°)
Density, lbs./gal.	6.9	107	57.5	7.6	8.7	8.3
Specific heat, cal./gm.	.33 (100° C.)	.033 (20°)	.058 (250°)	0.5±	.559 (300°)	1.0
Thermal conductivity	0.21	0.02	0.15	0.004	....	0.0013
Viscosity coefficient..	....	0.01 (200-300°)	0.01± (250°)	1.0±	....	0.010 (20°)
Heat of vaporization, cal./gm.	1100	65	621	....	74.4	539

Sodium Peroxide. Sodium peroxide, Na_2O_2, a white powder, is made from sodium, in two stages. First, the metal is placed in a revolving drum with dehydrated air passing over it; sodium oxide, Na_2O, also a white solid, is formed. This white powder is transferred to a second revolving drum, set in brickwork so that heat may be applied. Dry oxygen is passed into the heated drum, until no more is absorbed; the product now is the peroxide, Na_2O_2. It is valuable as an oxidizing agent for a number of minor chemical operations; in the bleaching of textile and pulp and paper stock; sometimes to make hydrogen peroxide. It serves to make zinc peroxide, calcium peroxide, magnesium peroxide, sodium perborate, urea peroxide, and other organic peroxides as for example benzoyl peroxide, a white powder. The latter agent functions as a catalyst, and as a bleaching agent for white flour ("Lucidol";[22] diluted with calcium phosphate, "Novadelox"[23]).

$$2C_6H_5\cdot CO\cdot Cl + Na_2O_2 \rightarrow C_6H_5\cdot CO\cdot O\cdot O\cdot OC\cdot C_6H_5 + 2NaCl$$

benzoyl chloride — a liquid; *benzoyl peroxide* — a solid

Part of the bleaching of flour was done by means of NCl_3, known as the Agene process. After mid 1949, this substance is banned. In its place, in part at least, chlorine dioxide ClO_2, made from sodium chlorite by chlorination

$$2NaClO_2 + Cl_2 \rightarrow 2NaCl + 2ClO_2$$

in special apparatus, in a wet process[23a] or a dry process,[23b] will be used.

[21] Sodium has been used as a liquid partly filling the hollow stem of the valve in an airplane motor, in order to dissipate heat which otherwise would have no escape.

[22] U. S. Pat. 1,380,334. [23] U. S. Pat. 1,381,079.

[23a] U. S. Pat. 2,131,447.

[23b] U. S. Pat. 2,309,457; see also *Ind. Eng. Chem.*, 37, 813 (1945).

Sodamide, Sodium Cyanide. Sodamide, a white solid, is made by the action of dry ammonia on metallic sodium; it is important in the synthesis of indigo, and in other organic reactions.

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$

Heated with carbon to 800° C. (1472° F.), sodamide is changed[24] to sodium cyanide

$$2NaNH_2 + 2C \rightarrow 2NaCN + 2H_2$$

sodamide — *sodium cyanide*, a solid

which is liquid at the furnace temperature and is run off as such; it may be cast into convenient shapes (cyanide egg). When making sodium cyanide, the two reactions are cast into one. A batch of 10,000 pounds of melted sodium is placed in a welded rolled steel retort, 5200 pounds of prepared charcoal added gradually, and 7400 pounds of ammonia passed in. An excess of carbon over the sodamide present at any one time is maintained. The escaping hydrogen provides the agitation. The high temperature is provided by three internal U-tubes, in which fire gases travel, or in some other way. Hydrogen passes out and, by means of a heat exchanger surmounting the retort, gives up much of its heat to the incoming ammonia. The hydrogen gas is reused in a synthetic ammonia plant. Only a small part of it is wasted by burning, at the end of a run. The melted cyanide may, if preferred, be flaked on a cold, rotating drum.

Sodium cyanide is used in electroplating; in fumigation; in the manufacture of dye intermediates and other chemical compounds; in the extraction of gold, silver, zinc and lead from its ores; in a mixture with sodium chloride and sodium carbonate, for the case-hardening of steel.

Reduction of Esters. The reduction of esters to produce paraffinic or olefinic alcohol, eagerly sought for the manufacture of detergents, is brought about by the theoretical weight of sodium dispersed in an inert solvent (toluene), in the presence of a slowly reacting alcohol, such as methyl amyl alcohol.[25] Any unsaturation in the charge is not disturbed. For the reaction below, ethyl alcohol will be written:

$$C_{15}H_{31}\cdot CO\cdot OC_2H_5 + 4Na + 3C_2H_5OH \rightarrow C_{15}H_{31}\cdot CH_2OH + 4C_2H_5ONa$$

ethyl palmitate — *cetyl alcohol*

The sodium is recovered by hydrolysis as sodium hydroxide; the alcohol, if properly chosen, may be recovered not far from the anhydrous state.

Sodium hydride, NaH, is a free-flowing, grayish-white powder, produced by hydrogen over sodium at 250-300° C. (482-572° F.), with the gas at the pressure of 1 atmosphere.[26]

Potassium Permanganate

The step in the manufacture of potassium permanganate which may be

[24] German Pat. 148,045.

[25] "Sodium reduction of fatty acid esters," V. L. Hansley, *Ind. Eng. Chem.*, 39, 55 (1947).

[26] "The production of sodium hydride and some of its reactions," V. L. Hansley and P. J. Carlisle, *Chem. Eng. News*, 23, 1332 (1945).

performed in an electrolytic cell is the change, in water solution, of potassium manganate, which is green, to potassium permanganate, which is red; this change is an oxidation, and takes place at the anode. The liquor at the same time becomes alkaline, because of the formation of potassium hydroxide. A cell which has been found suitable has a rotating anode of iron screening through which the liquor is made to flow. The oxidation reaction is:

$$2K_2MnO_4 + 2H_2O \rightarrow 2\ KMnO_4 + 2KOH + H_2$$

potassium manganate (green) — *potassium permanganate* (red)

The complete process of manufacture comprises a fusion of manganese dioxide, MnO_2 (pyrolusite), with caustic potash, KOH, in a muffle furnace with circulation of air. The furnace product is leached with water, treated to remove excess caustic potash, and passed through the cell. The potassium permanganate is so insoluble that some of it separates in the cell; on concentration, another part is obtained.

Another procedure independent of current consists in passing carbon dioxide into the manganate solution, with the formation of permanganate and hydrated manganese dioxide (artificial pyrolusite) as a by-product.

$$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3.$$

Still another is the treatment of the permanganate solution with chlorine.

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl.$$

Potassium dichromate may also be made with the aid of the electrolytic cell. In general, however, it is made in the standard way. The ore, chromite, is crushed, powdered, and fused with alkali carbonate in the presence of air; the cooled melt is leached, and the chromate allowed to crystallize. The dichromate is made by treating the chromate with a mineral acid.

Chromic acid in red crystal form is made by treating the chromate or dichromate with sulfuric acid of high concentration, and filtering through filtros or wool felt.

Ammonium Persulfate. Ammonium persulfate, $(NH_4)_2S_2O_8$, a white, crystalline solid only slightly soluble in water, is made by the electrolysis of a water solution of ammonium sulfate containing sulfuric acid. The anode is a small platinum plate (hence high current density), the cathode a larger lead plate (hence low current density); the bath is kept cold by cooling coils in which brine circulates (10° C.). The ammonium persulfate appears at the anode where it precipitates. This product is useful as an oxidizer for many minor purposes, as a catalyst in polymerizations, and as a solvent for silver in photography.

Sodium chlorate is produced by anodic oxidation of a solution of sodium chloride in cells without diaphragm, with graphite anodes and steel cathodes. The pH is kept below 7, and an addition of sodium chromate must be made (2 grams per liter). In the continuous process, a portion of the cell liquor

is diverted; part of its chlorate is crystallized, and the mother liquor, fortified with an equivalent amount of sodium chloride, is returned to the cell.

Sodium chlorate is used chiefly as a weed killer. The production is about 13,000 tons per year.

Much of the potassium chlorate is made by converting sodium chlorate to the potassium salt by double decomposition with potassium chloride. The production is about 12,000 tons per year. The bulk of the potassium chlorate is used in the manufacture of matches.[27]

Hydrogen Peroxide

Hydrogen peroxide, H_2O_2 until recently, entered the chemical market in the form of a water solution containing 27.5 per cent, 30 per cent, and 35 per cent peroxide. During World War II, a highly concentrated form containing 85 to 90 per cent hydrogen peroxide was developed, very largely in Germany, for war purposes. Since the war, this high-strength product has appeared on the American market; it is made from the 30 per cent solution by concentration.

Hydrogen peroxide is made by a variety of methods. For steady, large-scale production, the electrolytic methods are used. In one of these, sulfuric acid is oxidized, at the anode of the cell, to persulfuric acid. The latter is withdrawn from the terminal cell, along with unchanged sulfuric acid and water, and heated, under a reduced pressure, when it hydrolyzes, and produces a distillate consisting of hydrogen peroxide and water. The residual acid, not plain sulfuric acid, is diluted to a preferred strength, such as specific gravity 1.4, and is used over again. The hydrogen is allowed to escape to the atmosphere. The cells are generally diaphragm cells, with an asbestos or other partition wall separating the anolyte from the catholyte liquor. They must be operated at a temperature below 30° C. (86° F.); therefore cooling must be provided. A number of cells are connected to form a series; the anolyte liquor from one cell passes through piping (lead) laid in cold or refrigerated water, to the anode chamber of the next cell. Similarly, the catholyte liquor from one cell travels to the cathode chamber of the next, also with a cooling step. In each cell the concentration of the persulfuric acid rises. The cell reaction is:

$$\underset{\text{at anode}}{2HSO_4^- - 2 \text{ electrons}} \rightarrow \underset{\substack{\textit{persulfuric}\\ \textit{acid}}}{H_2S_2O_8} \; ; \; \underset{\text{at cathode}}{2H^+ + 2 \text{ electrons}} \rightarrow \underset{\text{gas}}{H_2}$$

The hydrolysis of persulfuric acid may be represented as follows:

$$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$$

The anolyte liquor is joined to the still residue and, like the latter, is reused. The operation of the cells is continuous; fresh acid of the proper strength enters the first cell in a series in a continuous stream; catholyte and anolyte travel from cell to cell continuously, and the catholyte effluent from the terminal cell rich in persulfuric acid is discharged in a continuous flow.

[27] "Electrolytic production of chlorates," N. C. White, The Electrochemical Society, 92, preprint, 1947. "Chlorates and perchlorates," J. C. Schumacher, *Chem. Eng. Progress*, 43, 177 (1947).

There is also the ammonium persulfuric process, shown in the over-all reactions below:

$$(NH_4)_2SO_4 + H_2SO_4 \rightarrow 2NH_4HSO_4$$
$$2NH_4HSO_4 \rightarrow (NH_4)_2S_2O_8 + H_2$$
$$(NH_4)_2S_2O_8 + H_2SO_4 \rightarrow H_2S_2O_8 + (NH_4)_2SO_4$$
$$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$$

The ammonium sulfate liberated in the third reaction and the sulfuric acid formed in the hydrolysis step are used over again; the process is continuous.[28] Theoretically, at least, only water and electrical energy are consumed; in practice a small amount of make-up material is required.

In still another method, the ammonium persulfate formed in the cell is reacted with potassium acid sulfate, $KHSO_4$, to give the rather insoluble potassium persulfate, regenerating the ammonium acid sulfate for return to the cell. It is the potassium persulfate which is then hydrolyzed to give the hydrogen peroxide solution (35 per cent H_2O_2, after distillation, for example), with regeneration of potassium acid sulfate:

$$(NH_4)_2S_2O_8 + 2KHSO_4 \rightarrow K_2S_2O_8 + 2NH_4HSO_4$$
$$K_2S_2O_8 + 2H_2O \xrightarrow{\text{as live steam}} 2KHSO_4 + H_2O_2$$

The potassium persulfate process [29] was operated in Germany in porcelain cells 3 feet long by 2 feet 3 inches wide, with a depth of 3 feet 1 inch. A current of 230 volts, 5,400 amperes, was applied to a bank of 40 cells; hence the voltage per cell was 5.75. The current efficiency was 85 per cent. Each cell contained six blocks of electrodes; each block consisted of 14 platinum wire anodes supported by rubber-covered aluminum tubing and surrounded by graphite rods; a cathode was wound with blue asbestos rope which formed the diaphragm. The cooling of the cell liquor was by means of internal glass cooling coils. The effective minimum distance between anode and cathode was 5 mm. The potassium persulfate was hydrolyzed in a porcelain retort and the vapors rectified at a pressure of about 38 mm. of mercury, producing a 35 per cent hydrogen peroxide solution. The latter solution, and similar ones from other processes, formed the starting point for the preparation of 90 per cent hydrogen peroxide.

In the processes just described, filtration steps have been omitted, as well as purification steps which remove not only suspended fine particles, but also traces of iron, platinum, and other metals. Hydrogen peroxide solutions of any strength are the more stable, the purer they are. The pH has an effect, in that low pH favors stability; two of the prominent brands of peroxide have a pH of 2 and of 4, respectively. Certain substances have been found to inhibit the decomposition of peroxide, and are therefore added in certain operations (see page 363).

Besides the electrolytic methods, which account for the bulk of the production, hydrogen peroxide may also be made by chemical methods, of

[28] U. S. Pat. 1,234,380.

[29] "Axis manufacture of hydrogen peroxide," Commander R. A. Cooley, U.S.N.R., *Chem. Ind.*, 58, 957 (1946).

which two will be described. The barium peroxide method retains some importance only because it has a salable by-product, blanc fixe. Barium oxide is heated to 600° C. (1112° F.), and dry air is passed over it; the barium peroxide, BaO_2, which forms, is cooled, and then treated with a moderate amount of steam. The resulting suspension, essentially of formula $BaO_2 \cdot 8H_2O$, is fed into dilute sulfuric acid containing some phosphoric acid; hydrogen peroxide is liberated and barium sulfate (blanc fixe [30]) precipitates. The latter is filter-pressed, washed and sold wet to paper mills. The solution of hydrogen peroxide is adjusted to proper strength by distillation.

The second chemical method consists of treating sodium peroxide in solution with sulfuric acid. The sodium sulfate formed is soluble, and is removed from solution by adding sodium fluoride and cooling to −2° C. (28.4° F.). The supernatant solution of hydrogen peroxide still contains about 3 per cent of mineral matter, which however does not generally interfere with its applications.

The 27.5 per cent hydrogen peroxide is also labeled "100 volumes," because one volume of the liquid liberates 100 volumes of oxygen under specified treatment; similarly the 3 per cent solution, the U.S.P. pharmaceutical strength, is "10 volumes." This strength, which may be prepared by diluting the higher strengths, may be stabilized with a small amount of acetanilide to reduce the tendency to liberate oxygen during long storage. Its value as a disinfectant is due to the quick liberation of oxygen when applied.

Hydrogen peroxide has become a valuable bleaching agent in textile finishing mills,[31] and for bleaching fur, wood, oils and fats and many other materials. After the agent has done its work, there is no residual matter other than water. It replaces sodium peroxide when needed in many of the latter's uses. The 27.5 and 35 per cent strengths are shipped in glass carboys, aluminum drums, aluminum tank trucks, and aluminum tank cars (as large as 75,000 pounds). The 100-volume grade was quoted at 19½ cents per pound in late 1948. The annual production may be estimated at between 25 and 30 millions pounds, on the basis of 30 per cent H_2O_2.

There are a number of other potential methods for the preparation of hydrogen peroxide. One of them involves reduction, followed by oxidation, of 2-ethyl anthraquinone; another the direct union of hydrogen and oxygen.

Concentrated Hydrogen Peroxide

Concentrated hydrogen peroxide, with 80 per cent H_2O_2 and higher, is a liquid which to the eye does not differ from pure water. It is made, as previously said, by concentrating the 30 and 35 per cent product of the electrolytic cell. The large-scale production of this material by the Germans in the war years of 1943 to 1945 represents a noteworthy advance in chemical technology. A typical plant [29] consisted of two units, each one equipped with a steam-heated still, a separator, and a rectifier. In the first unit, a still liquor with 73 per cent H_2O_2 was gently boiled, producing a distillate

[30] Chapter 31.

[31] "Continuous peroxide bleaching," *American Dyestuff Reporter*, in 4 parts, Aug. 14 to Sept. 25, 1944. A rate of 250 yards a minute is given.

with 65 per cent H_2O_2. Fed to the still of the second unit, the 65 per cent material produced a liquid in the still containing 80 per cent H_2O_2. The rectifier furnished 56 per cent liquor, which was returned to the second still. Both stills and columns were porcelain, as were the Raschig ring packing of separators and rectifiers; the condensers were aluminum, and the cooling coils, stainless steel (18% Cr, 8% Ni, 5% Mo). The adjoined schematic

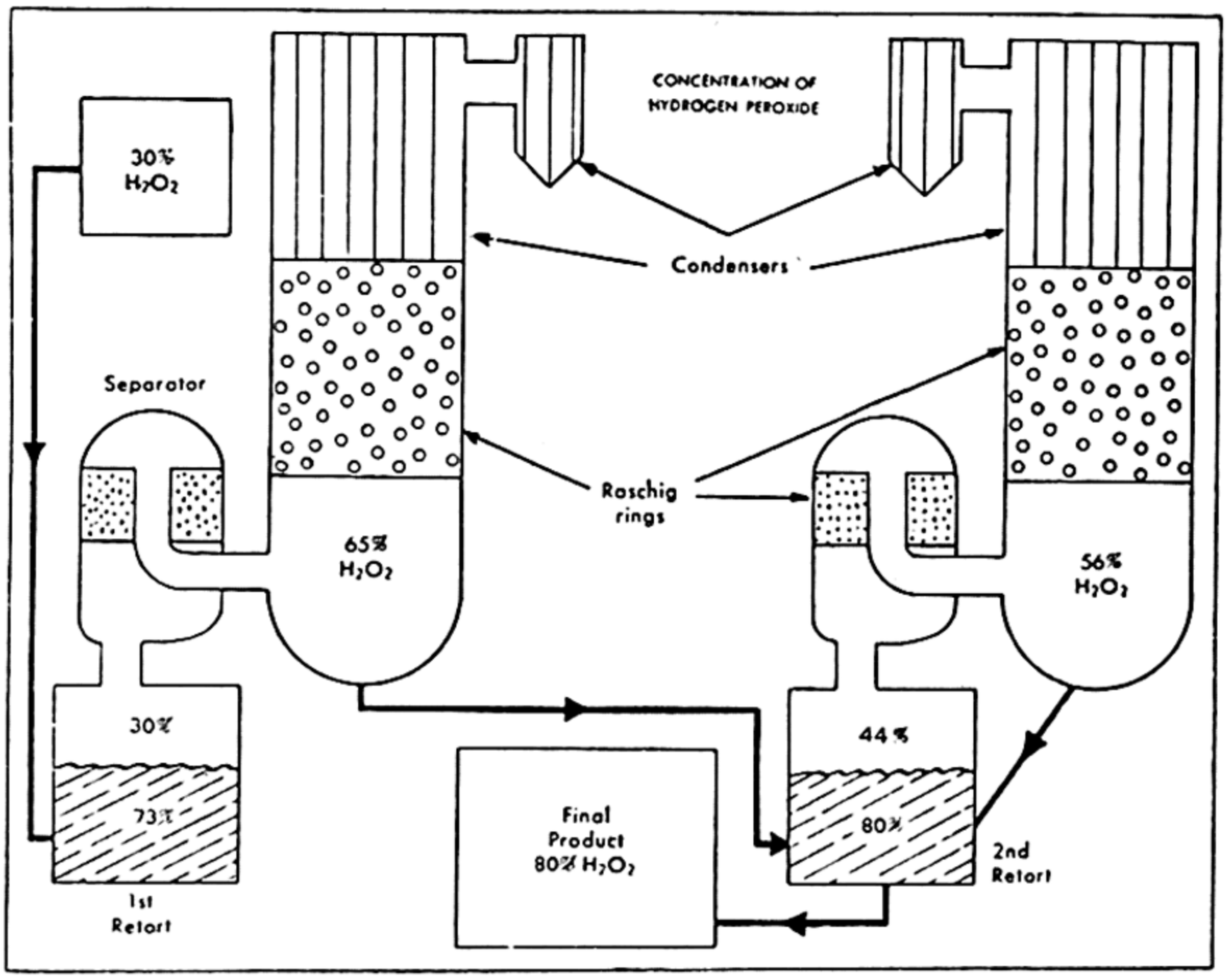


FIGURE 144.—Flowsheet for the concentration of 30 per cent hydrogen peroxide to 80 per cent, in a German plant. Steam jet ejectors at upper right of first unit and upper left of second unit not shown. (*Chemical Industries*, 58, 959.) (By permission.)

sketch represents the operations at the Schickert plant at Bad Lauterberg; its capacity was 1200 metric tons of 80 to 90 per cent H_2O_2 a month. The total German capacity in 1944 was 5800 metric tons per month, actual, with plans well advanced for 10,000 tons.

TABLE 57.—*Summary of the Two Units for Manufacturing 80 to 90 Per Cent Hydrogen Peroxide.*[29]

	First Unit	Second Unit
Temp. of liquor in the still	66° C.	75° C.
Pressure	40 mm Hg	40 mm Hg
Liquid in still	73% H_2O_2	80% H_2O_2
Vapor phase	30% H_2O_2	44% H_2O_2
Bottoms, rectifier	65% H_2O_2	—
Product	—	80% H_2O_2

The vapor pressure of hydrogen peroxide at any temperature is lower than that of water.

The original 35 per cent product from the electrolytic cell is treated with ammonia to reduce its free sulfuric acid content to 0.5 gram per liter, with 120 milligrams of ammonium pyrophosphate per liter as stabilizer, before delivering it to the first unit. It will be noted that the double unit provides for the retention of non-volatile impurities in the first still; the distillate is free from them. After about a week's operation, the solids accumulated in the still residue (80 grams per liter) are removed by draining the still and washing it. The 80 per cent product leaving the second still is cooled, and then passes to storage, after the addition of 23 milligrams of phosphoric acid (87%) as stabilizer.[29] The over-all efficiency for the concentration of 35 per cent hydrogen peroxide to the 80 to 90 per cent was 98 per cent.

Concentrated hydrogen peroxide in contact with permanganate and other catalysts decomposes to oxygen and steam. One pound of 90 per cent hydrogen peroxide releases approximately 1110 Btu.; the temperature rise under adiabatic conditions will be approximately 1320° F. at atmospheric pressure.[32] The heat released is sufficient to convert the products into superheated vapor. One volume of the same 90 per cent peroxide will produce about 5000 volumes of superheated vapors at atmospheric pressure. These relationships were utilized in different ways; for launching V-1 bombs, for driving fuel pumps in V-1 bombs, for driving torpedoes, ME 163 and 262 airplanes, and submarines—for 26 war weapons in all. In addition, 40 other weapons using peroxide were in the experimental stage.[33]

In this country, concentrated hydrogen peroxide for peace time uses, is available, and is shipped in vented aluminum drums which should be shielded from the sun; it is practically a new substance with properties of its own, and it is expected that many new and original uses will be developed. Spills must be flushed at once with large amounts of water. Contact with iron and copper must be avoided.

TABLE 58.—*Specific gravity of hydrogen peroxide solutions.*

H_2O_2		
27.5%	1.1026	at 20° C.
30	1.11	at 18
35	1.1322	at 20
50	1.198	at 18
90	1.39	at 18

OTHER PATENTS

U. S. Patent 1,839,756, on an apparatus (cell) for electrolyzing fused NaCl, and 1,826,773, on the method of salt feed; on the collection of magnesium in the cell, German Patents 344,427 and 302,024; on the electrolysis of NaOH for sodium, German Patents 344,427 and 302,024; U. S. Patent 1,875,760, electrolysis of molten magnesium chloride; 1,820,022, production of metallic magnesium by electrolysis of fused $MgCl_2$; 1,878,939, metallic aluminum by thermal reduction of oxide ores; 1,833,806, electrolytic refining of aluminum; 1,770,940, chemically pure aluminum by electrolysis; 2,021,384,

[32] "The development, manufacture, properties and applications of high concentrated hydrogen peroxide," George Crewson and Noah S. Davis, Jr., (Becco), an address delivered at the Buffalo meeting, 1948, of the Am. Inst. Chem. Inst., but not published.

[33] See Chapter 33 for further information, and for reading references.

removal of acid from peroxide solutions, to Joseph Reichert; 2,008,726, storing and handling hydrogen peroxide solution; 2,004,809, 2,022,860, on stabilizing hydrogen peroxide; 2,017,440, on hydrogen peroxide purification; 2,022,650, on hydrogen peroxide process; 2,054,303, on the reaction of sodium with hydrocarbons, to Norman D. Scott; 2,065,744, on the production of sodium perborate; U. S. Patent 1,921,377, the Ward magnesium and chlorine cell. U. S. Pat. 1,996,471, preparation of acyloins; 2,015,040, direct union of hydrogen and oxygen to form hydrogen peroxide; also 2,416,156. Dutch Pat. 58,703, hydrogen peroxide from amalgams, and 52,521, from hydrocarbons. U. S. Pat. 2,416,550-1, on producing chromate.

Problems

1. An aluminum furnace is to produce 120 pounds of metal per day. How much alumina will be required, if the yield is perfect, and how much carbon will be consumed at the anode if reaction (2) given in the text takes place exclusively?

2. Sea water contains 0.48 per cent $MgCl_2$. In order to produce one ton of magnesium, how many gallons of sea water must be treated with lime to produce magnesium hydroxide, and how much lime and how much hydroxide will be involved? How much chloride will be formed from the hydroxide, ready for the cell? The recovery in each case may be assumed to be 100 per cent.

3. A bank of 20 cells produces 6 tons of sodium per day. The feed is purified sodium chloride, and is steady throughout the day. How much NaCl per hour must be fed into the 20 cells, and how many pounds of chlorine will be collected? Let the sodium recovery be perfect, and the chlorine recovery be 92 per cent.

4. The decomposition voltage in the electrolytic cell is found by means of the expression $E = Q \times 4.1834 \div [96580 \times n]$, in which E is in volts; n is the number of gram equivalents involved; Q is the heat of formation of all the substances taking part in the reaction, the heat for the substances on the left being taken as positive, while the heat for those on the right are taken as negative. This first value of Q must be corrected for the heat already present in the fused substances in the electrolytic furnace. The mole heat (which is the product of specific heat and molecular weight) in calories, for each substance on the left of the reaction (here a single substance) is deducted from the Q value, also in calories, originally found; the reduced value serves to compute E. Apply to fused salt NaCl, at 600° C. cell bath temperature.

Heat of formation of solid NaCl, 58.46 grams		97,700 gr. cal.
Heat of fusion, at the melting point, 804° C.	7200 gr. cal.	
Heat of the melt at 600° C. = 585 × 13.33	7798	
		− 14,818
		82,882

$[82{,}882 \times 4.1834] \div [96{,}580 \times 1] = 3.59$ volts $= E$

The decomposition voltage of sodium chloride fused at 600° C. is 3.59 volts.

5. The heat of formation at 15° C. of $MgCl_2$ is 151,000 calories. Its mole heat is 18.5. The electrolytic decomposition is performed at 700° C. The heat of fusion is 7000 cal. (est.). What is the decomposition voltage, remembering that $n = 2$? Compare with the figure in the text.

6. The heat of formation of Al_2O_3 is 378,000 calories. The heat of formation of CO is 26,200 calories. The heat of fusion of alumina is 5188 calories for the mole. If electrolysis takes place at 915° C., and the mole heat of alumina is 20.4, what is the decomposition voltage for the reaction $Al_2O_3 + 3C \rightarrow 2Al + 3CO$? What is the decomposition voltage if the reaction is $Al_2O_3 + 1\frac{1}{2}C \rightarrow 2Al + 1\frac{1}{2}CO_2$? The heat of formation of CO_2 is 94,200 calories. Answer: For the first reaction, 1.99 v.; for the second, 1.54 v.

7. What are the theoretical weights of the metals deposited per faraday (96.580 coulombs) for the metals in problems 4, 5 and 6, and what are the weights of the several salts decomposed by one faraday? What are the actual weights of these salts so decomposed, taking into account the current efficiency stated in the text?

Solution for problem 5

Heat of formation of $MgCl_2$			151,000 calories
Heat of the bath, if all $MgCl_2$	$18.5 \times 685 =$	12,672	
Heat of fusion of $MgCl_2$ (est.)		7,000	
		19,672	19,672
			131,328

$$[131{,}328 \times 4.1834] \div [2 \times 96{,}580] = 2.84 \text{ volts.}$$

Solution for problem 6

First reaction $Al_2O_3 + 3C \rightarrow 2Al + 3CO$ at 915° C.

Heat of formation of alumina			378,000 calories
Heat of formation of 3CO	$3 \times 26{,}200 =$	78,600	
Heat of the alumina in cell bath	$20.4 \times 900 =$	18,360	
Heat of fusion	$50.9 \times 101.94 =$	5,188	
		102,148	102,148
			275,852

$$[275{,}852 \times 4.1834] \div [6 \times 96{,}580] = 1.99 \text{ volts.}$$

Second reaction $Al_2O_3 + 1\frac{1}{2}C \rightarrow 2Al + 1\frac{1}{2}CO_2$

Heat of formation of alumina		378,000 calories
Heat of formation of $1\frac{1}{2}CO_2$	141,300	
Heat of alumina in cell bath	18,360	
Heat of fusion	5,188	
	164,848	164,848
		213,152

$$[213{,}152 \times 4.1834] \div [6 \times 96{,}580] = 1.55 \text{ volts.}$$

Reading References

"The principles of applied electrochemistry," A. J. Allmand and H. J. T. Ellingham, London, Edward Arnold & Co., 1924, p. 520-528.

"Metallurgy of aluminum and aluminum alloys," R. J. Anderson, New York, H. C. Baird & Co., 1925.

"Hydropower for the production of aluminum," James W. Rickey, *Trans. Electrochem. Soc.*, 70, 185 (1936).

"Recent advances in the aluminum industry," Francis C. Frary, *Trans. Electrochem. Soc.*, 70, 131 (1936).

"The Aluminum Industry," J. D. Edwards, Francis C. Frary, and Zay Jeffries, 2 volumes, McGraw-Hill Book Co., New York, 1930.

"Making alumina at Mobile," James A. Lee, *Chem. Met. Eng.*, 47, 674 (1940), with an attractive flow sheet.

"Economics of the aluminum industry, Francis C. Frary, *Ind. Eng. Chem.*, 28, 146 (1936).

"How Europe produces its magnesium," Ernest V. Pannell, *Chem. Met. Eng.*, 48, 78 (1941).

"Magnesium: its production and use," Herbert A. Francke, *Chem. Met. Eng.*, 48, 75 (1941).

"Magnesium by the Hansgirg Process," Sidney D. Kirkpatrick, *Chem. Met. Eng.*, 48, 91 (1941), with six photographs.

"The magnesium industry," John A. Gann, *Trans. Am. Inst. Chem. Eng.*, 24, 206 (1930).

"Magnesium metal and compounds," Paul D. V. Manning, *Chem. Met. Eng.*, 45, 478 (1938), with two flow sheets, one starting from bittern, one from sea water.

"Magnesium in the national defense," L. B. Grant, *Trans. Am. Inst. Chem. Eng.*, 37, 489 (1941); appeared also in The Monthly Review of the American Electroplaters Society, November 1941, p. 869.

"Magnesium from the sea," D. H. Killeffer, *News Edition* (Am. Chem. Soc.), 19, 1189-1193 (1941), illustrated, flow sheet.

"Producing chromate salts from domestic ores," an abstract of bulletin V of the State College of Washington, *Chem. Met. Eng.*, 47, 688 (1940).

"Theoretical and applied electrochemistry," 3rd ed., Maurice de Kay Thompson, New York, The Macmillan Company, 1939.

"The handling of sodium on the industrial scale with examples of its use in chemical reactions," P. J. Carlisle, *Trans. Am. Inst. Chem. Eng.*, 31, 316 (1935).

"Large scale production of metal hydrides," Herman W. Zabel, *Chem. Ind.*, 60, 37 (1947).

"The German hydrogen peroxide industry," Report P. B. 17331, Technical Industrial Intelligence Division, Office of Technical Services, Dept. Comm., Washington 25, D. C.

"An investigation of the commercial possibilities of metallic peroxides as a source of hydrogen peroxide," L. W. Blundell, *Trans. Inst. Chem. Eng. (London)*, 8, 191 (1930). The barium peroxide method, to produce dilute solutions.

The utilization of gases on the industrial scale is one of the triumphs of modern chemical engineering; the seamless steel cylinders in which some of them are transported, under pressure, are familiar sights on trucks and railway cars. Gases serve as chemical agents, refrigerants, anesthetics, disinfectants; they also serve in beverages, for flames, and to stifle flames.

Chapter 19

Industrial Gases

The gases included in this chapter fall into two groups: hydrogen, H_2, helium, He, oxygen, O_2, nitrogen, N_2, argon, A, and carbon monoxide, CO, the less easily liquefiable gases; and chlorine, Cl_2, sulfur dioxide, SO_2, ammonia, NH_3, nitrous oxide, N_2O, carbon dioxide, CO_2, and ethyl chloride, C_2H_5Cl, the more easily compressible gases. At ordinary temperatures, the former do not liquefy in spite of considerable pressure; the latter at ordinary temperatures form liquids under rather moderate pressures; hence the content by weight of a standard cylinder for the gases in the first group will be small, for those in the second group, considerable. It follows that gases in the first group are generally used as free gases as soon as they are generated, or will be shipped short distances, from many plants, each serving a small territory; whereas gases in the latter group may economically be shipped long distances, from a few central plants.

The distinction between the two groups is less sharp today, however. Even before World War II, oxygen in the liquid form was transported in tank cars and tank trucks, over short distances, as from one plant to another in the same city. To meet the urgent demands of the war, liquid oxygen as such was transported over distances as great as from Chicago to the West coast. Nitrogen similarly may be transported over great distances in the liquid state. For miscellaneous industrial uses, the familiar steel cylinder with its charge of compressed gas, remains standard.

Acetylene, C_2H_2, lies midway between the two groups; it is in a class by itself, partly because its explosive nature requires that special precautions be taken in handling it.

In addition to a variety of technical uses, several members of the second group serve as ordinary refrigerants—ammonia, carbon dioxide, sulfur dioxide, and ethyl chloride: to these must be added the newer refrigerants, dichlorodifluoromethane, propane, and butane, which are discussed in Chapter 12. Members of the first group are used as extraordinary refrigerants; for example, nitrogen in liquefaction of the carbon monoxide impurities in hydrogen.

Hydrogen

Of late years, hydrogen has become of industrial importance in the direct synthesis of ammonia, in the synthesis of hydrogen chloride, in the hydrogenation of fatty oils, of petroleum oil fractions, of coal, of hydrocarbons, of metallic hydrides, and single organic substances; its other uses are for balloons and dirigibles, and for hydrogen-air, hydrogen-oxygen, and atomic hydrogen flames.

It is obtained from water gas, producer gas, or coke-oven gas, by the removal of the non-hydrogen constituents; it is made by the catalytic action of steam on oil refinery gases and natural gas, by the thermal decomposition of natural gas, by steam on heated iron, by the electrolysis of water, and by miscellaneous processes. It is a by-product in the electrolytic cell for caustic,[1] in several fermentation processes, and in other types of processes. The choice of a process will be decided by the resources at hand, and by the degree of purity required. Rapid generation with a minimum of apparatus in an isolated place may be demanded; in such a case the steam-methanol process or the ferrosilicon process would serve.

The Water Gas and Steam Process, a Continuous Catalytic Process. Water gas with steam in excess is passed over an iron oxide catalyst, just as is done in the Bosch process described in Chapter 6, except that since no producer gas is added, the amount of nitrogen is small. The converter has several trays, on which the catalyst rests. The reaction

$$CO + H_2O \longrightarrow CO_2 + H_2$$

is exothermic; as the temperature must be maintained at 450° C. (842° F.), the converters are insulated and the incoming gases heated in exchangers. Once the reaction has begun, no outside fuel is required. Three volumes of steam to one of gas are used; the great excess of steam drives the reaction to the right. After passing the exchangers the reacted gas is freed from its steam by water-cooling. The carbon dioxide formed, as well as the small amount which entered with the water gas (4 per cent), is removed by scrubbing with cold water while under pressures of 25 to 30 atmospheres, in tall steel towers; under such pressures carbon dioxide is freely soluble in water. The gas leaving the last scrubber has the composition:

	Per cent
Hydrogen	92–94
Nitrogen	1–4
Methane	0.5
Carbon monoxide	2–4
Carbon dioxide	small
Moisture	small

The crude hydrogen may be further purified from carbon monoxide by scrubbing in ammoniacal cuprous chloride solution. The nitrogen impurity may be lowered by careful operation of the water-gas plant. The methane is not wanted, and may be almost avoided by using well-burned coke.

A similar process in which the catalytic agent is lime at the temperature of 450° C. (842° F.) instead of iron oxide has been proposed; its great advantage is that the carbon dioxide is simultaneously removed. Unfortunately this absorption is accompanied by a powdering of the lime granules, as the carbonate forms, and the powder tends to clog the lime towers.

Water Gas Process with Liquefaction of the Carbon Monoxide. There are two processes in which the carbon monoxide in water gas is liquefied by cold and pressure and removed in that state, leaving the hydrogen gas comparatively pure. The Linde-Fränkl-Caro process uses liquid air boiling under

[1] Hydrogen from mercury cells for caustic has a slight contamination of mercury, which for certain uses, must be removed [*Chem. Ind.*, 61, 44 (1947)].

a few millimeters of pressure for the final cooling of the water gas already precooled by three steps, first by an ammonia refrigerating system (−35° C. or −31° F.), then in an exchanger wherein the uncondensed hydrogen takes up heat, third by the liquid carbon monoxide separated in the final cooling. The carbon monoxide at the same time boils, and is used as a gaseous fuel. The other process is Claude's, which uses no liquid air, but obtains the necessary final cooling by the expansion of hydrogen from a pressure of 20 atmospheres to a lower pressure while doing work against a piston. The hydrogen is pre-cooled in exchangers by outgoing gases, and by the evaporation of the carbon monoxide which has been previously liquefied.

The hydrogen in coke-oven gas,[2] and in the gas from petroleum-cracking stills may be recovered by liquefaction of the non-hydrogen components.

Steam on Heated Iron. The interaction of steam and iron takes place at an elevated temperature, such as 650° C. (1202° F.) in a multiplicity of relatively small, upright steel cylindrical retorts. The iron packing is selected so as to have a porous structure and little tendency to disintegrate; a calcined iron carbonate (spathic ore) has been found suitable. A plant for the production of 3500 cubic feet (about 100 cubic meters) per hour would consist of three sets of 12 retorts each, each retort being 9 inches in diameter and 12 feet high. The action is intermittent. The steaming period (hydrogen production) lasts 10 minutes (upward travel of steam).

$$3Fe + 4H_2O \rightarrow Fe_2O_3 + 4H_2$$

The iron oxide formed is reduced by water gas, for example, and the water gas period lasts 20 minutes (downward travel), because the reduction of the oxide is slower than the oxidation of the iron. A brief purging with steam sends the first hydrogen to the water gas holder. By the stepwise operation of such a plant a continuous flow of hydrogen is obtained. The spent water gas is cooled and burned (for it still contains combustible gases) around the retorts to maintain the reaction temperature. The steam reaction is exothermic; the over-all reduction by the water gas is endothermic.

The hydrogen passes out with the great excess of steam which is employed to drive the reaction to the right; it is cooled to remove the steam, and freed from carbon dioxide and hydrogen sulfide by lime purifiers. The gas obtained is 98.5 to 99 per cent pure; by careful purging, using closed condensers instead of scrubbing towers, and other modifications, the purity may be raised to 99.94 per cent. The steam-iron process is used chiefly in connection with the hydrogenation of fatty oils. The iron mass lasts six months, the retorts one year.

For the production of 1 volume of hydrogen, the continuous catalytic process requires 1.25 volumes of water gas, the liquefaction process (CO liquefied) 2.5 volumes, and the steam-on-heated-iron process, also 2.5 volumes.

Electrolysis of Water. In commercial cells, the direct current is passed between iron electrodes, which may be nickel-plated, suspended in a bath consisting of a 10 to 25 per cent caustic soda or potassium hydroxide solution. Only distilled water is added to the cells, for the electrolyte is not

[2] Chapter 15; and *Ind. Eng. Chem.*, 14, 1118 (1922).

consumed. Cells differ in the method of gathering the hydrogen (at cathode) and the oxygen (at anode), in size, and in details of construction. The efficiency is close to 7.5 cubic feet of hydrogen per kilowatt hour, and 3.8 cubic feet of oxygen. The cost of hydrogen depends mainly on the cost of the electric power. If the horsepower year is $20, a low figure generally, 1000 cubic feet of hydrogen will require 40 cents just for power, assuming that the oxygen is wasted. The continuous catalytic process produces 1000 cubic feet of hydrogen for about 45 cents, granted favorable conditions for coke and coal.

The decomposition voltage for the reaction $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ is 1.48; the operating voltage about 2. The amperage varies with the size and intensity of operation; with maximum load, it may be as much as 1000 amperes for electrodes 40 inches wide and 60 inches high, with a number of electrodes in each cell. The electrodes are separated by an asbestos diaphragm, and suspended in cast-iron containers.

One of the large-scale installations[3] for the electrolytic production of hydrogen consists of 306 cells, each with 20 plates. The electrolyte is 25 per cent very pure potassium hydroxide, maintained at 60° C. (140° F.) by the Knowles patented regulator. Each electrode receives 500 amperes, hence 10,000 amperes per cell. The production is 49,000 cubic feet of hydrogen per hour, 99.5 per cent pure, and half that quantity of oxygen. This gas is used in making synthetic ammonia, as part of large auxiliary plants for the manufacture of chemical fertilizer.

Cells operating under pressure and delivering gas at 200 atmospheres have been proposed; the energy required for electrolysis decreases as the pressure is increased.[4]

Other Processes and By-product Hydrogen. Hydrogen gas is prepared by the thermal decomposition[5] of natural gas, particularly in California, where the state law prohibits the wasting of natural gas. The operation is a cracking of the gas, and is performed in apparatus similar to those used for making water gas. A five-minute cycle is used: the gas is burned to heat up the checkerwork in the generator (2 min.); then the gas, without air, is passed in. Elemental hydrogen gas with suspended carbon particles forms; the carbon is filtered out in bag filters. After 2 minutes, the generator is too cool, and the cycle is repeated.

In the oil industry, hydrogen may be prepared from hydrocarbons in the refinery gases, or in available natural gas, by treating with steam, with or without a catalyst. The reaction is

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2.^{6}$$

For the reaction

$$CH_4 + H_2O \rightarrow CO + H_2,$$

the catalyst nickel-magnesia, and the temperature 800° C. are suitable.

[3] Knowles hydrogen plant at Warfield Works, Consolidated Mining and Smelting Company, of Canada, *J. Soc. Chem. Ind.*, 51, 355 (1932).
[4] *Trans. Inst. Chem. Eng. (Brit.)*, 9, 154 (1931).
[5] *Chem. Met. Eng.*, 39, 381 (1932).
[6] *Ind. Eng. Chem.*, 22, 1030 (1930); *Trans. Am. Inst. Chem. Eng.*, 41, 453 (1945).

The by-product hydrogen from the electrolytic caustic cell is discussed in Chapter 5; from fermentation[7] in Chapter 20; and its utilization in Chapter 25.

In the ferrosilicon process, powdered ferrosilicon containing as much silicon as possible (90 per cent is frequent) is added to a 20 per cent solution of caustic soda at a temperature of 80° to 90° C.; very pure hydrogen is produced. Aluminum in the form of shavings also gives hydrogen with a solution of caustic soda. An alloy of sodium and lead reacts with water to give hydrogen, again of high purity (hydrone). These three processes serve for military purposes and as supplementary plants for emergency or rapid operations. In addition to these, portable hydrogen manufacturing plants carried on trucks were built for Army use in the recent war, in which methanol and steam react catalytically to produce hydrogen and carbon dioxide. The reaction is exothermic, and outside heat is furnished by flue gases which pass through the converter, heating the outside of the catalyst-containing tubes. The temperature in the converter is 500° F. (260° C.). The carbon dioxide produced,

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2,$$

is scrubbed out in a monoethanolamine solution.[8]

Helium. This comparatively rare gas is produced in large quantities at Amarillo, Texas; it occurs in a number of natural gases in amounts varying from 0.5 to 7 per cent, averaging near 3 per cent. The gas is compressed and cooled, and the non-helium portion removed by liquefaction; 97 per cent He with some nitrogen is obtained.[9] Helium is used for dirigible balloons and observation blimps which rendered invaluable aid in the war; its value lies in the fact that it is inert, does not burn, and forms no explosive mixture with air. The risk in using hydrogen was underlined by the catastrophy to the Hindenberg, at Lakewood, N. J. (May, 1937). Yet large dirigibles, even though filled with helium (the *Macon, Shenandoah, Akron*) have proved failures from other causes. The lifting power of helium is 92 per cent of that of hydrogen.

The Heliarc welding process, originally a helium process, is described under argon.

A portable helium repurification plant has been designed.[10] It is estimated that the helium reserves already in sight are 10 billion cubic feet, in the United States alone. There is a potential production of 200,000 cubic feet per day from the gas in the boric acid fumaroles in Italy. Canada has some low percentage helium material.

Oxygen

The great importance of the industrial gas, oxygen, is due to the usefulness of the acetylene torch for steel welding and steel cutting, and for the

[7] *Ind. Eng. Chem.*, 18, 1045 (1926).
[8] *Trans. Am. Inst. Chem. Eng.*, 42, 396 (1946).
[9] "The production and uses of helium gas," by R. R. Bottoms, *Aeronautical Eng.*, (1929) (107; also *Ind. Eng. Chem.*, 11, 152 (1919).
[10] *Ind. Eng. Chem.*, 22, 1191 (1930).

welding of other metals; to a lesser degree to the oxyhydrogen flame. Oxygen gas in the breathing apparatus for aviators at high altitudes and for oxygen tents in hospitals is a more recent development. An extension of the use of oxygen lies in the increased intensity and speed of reactions brought about by oxygen-enriched air instead of ordinary air; the reduction of the cycle time so achieved in chemical or metallurgical processes permits a greater yield per volume of equipment, and brings about lower costs. Oxygen as a raw material for synthesizing chemical compounds is in daily use (ethylene oxide, sodium peroxide). Liquid oxygen mixed with carbon black may yet become an important and cheap explosive.

On the commercial scale, oxygen is made from atmospheric air; a small production by the electrolysis of water is the result of special circumstances. All processes based on atmospheric air involve two steps which are distinct even when combined in one piece of equipment: (1) the liquefaction of air (preceded by a purification), and (2) separation of the oxygen from the nitrogen by fractionating the liquid in a plate column.

Atmospheric air contains

	Per cent by volume	Per cent by weight
Nitrogen	78.03	75.5
Oxygen	20.99	23.1
Argon	0.933	1.29
Carbon dioxide	0.03	0.049
Water vapor (not included)	variable amounts	

In addition, air contains in smaller amounts, hydrogen and rare gases:

	Per cent by volume
Hydrogen	1×10^{-2}
Neon	1.5×10^{-3}
Helium	5×10^{-4}
Krypton	1.1×10^{-4}
Xenon	0.8×10^{-5}

For practical purposes, air may be considered a binary mixture, or solution, of nitrogen and oxygen.

The composition of liquid air varies slightly according to the conditions of liquefaction; on warming it, there passes out a gas containing 93 per cent nitrogen and 7 per cent oxygen, and there is left a liquid becoming gradually richer in oxygen, until at equilibrium with atmospheric air the liquid contains about 45 per cent oxygen. Nitrogen boils at −195.8° C., air at −191°, oxygen at −183.0°, all under a pressure of 1 atmosphere. The difference in boiling points of nitrogen and oxygen is not quite 13° C., the nitrogen being the more volatile. It is upon this fact that the fractionation is based. The oxygen produced, and also the nitrogen, may be drawn off in the form of a liquid, or they may be vaporized and collected in the form of a gas.

The various procedures for the production of oxygen may be represented by the four divisions which follow: (1) The old, small cycles, which produced oxygen in the form of gas; (2) the Heylandt liquid oxygen plant, which produces liquid nitrogen at the same time, by raising the working pressure; (3) The "Fränkl low-cost oxygen-in-the-form-of-gas" plant, or "tonnage

oxygen" plant; (4) the modern portable oxygen gas generators developed for the Army Air Corps during the war. Systems 1, 2 and 4 serve primarily for the production of 99.5 per cent purity oxygen.

The liquefaction of air is preceded by the removal of carbon dioxide, dust, and water vapor, and includes compression to high (or medium) pressure; cooling to low temperature in heat exchangers (or in recuperators); liquefaction by expansion, either without doing work (the Joule-Thomson effect, used in the early Linde system) or by doing work against a piston or a turbine wheel (the main feature of the Claude system). In the starting period, the equipment is brought from room temperature to the low temperature; in the running period, called the stationary period in Great Britain, the low temperatures are constant. After a long time, which varies with the type of plant from a week to as much as several months, the production is stopped and the apparatus warmed in order to thaw out and remove any solid carbon dioxide, hydrocarbons or water which escaped the purification system.

(1) In the old, small-cycle installations, the atmospheric air is drawn for the production of, for example, 15 cubic meters (530 cubic feet) of free oxygen per hour, into a four-stage compressor having four separate cylinders. After each compression, the air enters a coil set in running cold water so that it enters the next stage at room temperature. The rise in temperature for the compression is approximately the same for each of the four stages, to 170° C.

The carbon dioxide may be removed before reaching the compressor, by drawing the air through two towers working in series, filled with coke, down which a solution of caustic soda or caustic potash travels; the air passes up the tower, on the countercurrent principle. The tower packing rests on a false bottom; the liquor accumulates at the base and is circulated to the top of the tower by a small gear pump. Dust is caught at the same time. An alternative system is to remove the carbon dioxide in the compressed gas between the third and fourth stage.

Before entering the liquefying system, any water in the air must be removed, for water, like carbon dioxide, would deposit as a solid and plug the small pipes or the expansion valves. The amount of water brought in by the air is considerable. In a plant making 15 cubic meters of oxygen per hour, taking in 120 cubic meters of air per hour containing 65 per cent of the maximum humidity at 20° C., 193 kilograms [11] of water enter in a six-day period. The greater part of that water is removed by liquefaction as the air from the several cylinders is cooled, and run off before the air enters the next stage; only that contained in the fourth-stage air, estimated at 1.48 kilograms, needs to be absorbed by a special device. This consists best of a cylindrical vessel with false bottom filled with fused calcium chloride sticks. The air travels upward; the liquefied calcium chloride travels down and may be drawn off at intervals. Caustic potash may be used instead, and in that case its liquor can serve in the carbon dioxide-removing cylinders.

[11] One kilogram is 2.2 pounds.

The compression in the several stages is shown below, and at the same time the volume which at the pressures stated weigh 1 kilogram [11]:

Stages	1	2	3	4
pressure	4.1 atmospheres [12]	14.5	50	200
volume	86 liters	23.35	6.93	1.94

These pressures apply to the starting period; in the running period they are as stated in the table for the first three stages, but the fourth is about the same as the third. Advantage is taken of this fact to send in during the running period so-called low-pressure air (25 to 50 atmospheres) which liquefies easily at the temperature of the liquefier, which is very near −191° C.; in this way an important saving in power is made.

As a rule the liquefying vessel and the fractionating column are combined, thus avoiding a transference of the liquid. For plants producing more than 15 cubic feet of oxygen per hour, the gas from the fourth stage is precooled by an ammonia refrigerating system; when this is done the water is thereby removed, so that a calcium chloride tower is not needed, and at the same time the air enters the exchanger at a temperature of −30° C., thereby increasing the liquefying capacity of the system. With a single-column rectifier, the wasted gas is 93 per cent nitrogen and 7 per cent oxygen; the yield is 66 per cent. With a double-column rectifier, the escaping gas has only 2 per cent oxygen, and the yield is 90 per cent. The double-column rectifier is used in all the Linde systems, for medium and large daily production; slightly modified, it is part of the Heylandt liquid oxygen cycle. A description of the combined liquefier and separator with double column follows; a single-column rectifier would be the lower half.

The combined liquefier-rectifier provides for the interchange of heat in double coils, and the rectification of the liquid in the plate columns. Referring to Figure 145, the entering air passes through the inner coils of a double-walled coil system, while the outgoing oxygen and nitrogen surround them. The entering air loses heat to the outgoing gases, and it will be noted from the drawing that the coldest oxygen meets the air already cooled in the upper coils; the warm entering air, on the other hand, can still lose heat to the oxygen (and nitrogen) which has passed through all the coils and is ready to leave the system. The compressed air thus reaches the coil in the base of the column well precooled; it cools still further in contact with the liquid in the column, and when it reaches the expansion valve, it liquefies readily. This accomplished, the two constituents are separated by permitting the liquid to drop from shelf to shelf, in contact with the rising gas. At each shelf, an interchange takes place; the liquid loses a part of its more volatile constituent, nitrogen, and robs the gas of a part of its less volatile constituent, oxygen, so that the liquid which reaches the lower shelf is richer in oxygen than the liquid on the shelf just above it. The separation is continued in the upper column, as indicated in the illustration.[13] As the liquid from the lower column at 4 enters the shelves in the upper column, and

[12] One atmosphere is 14.70 pounds per square inch.

[13] Shelves with bells providing liquid seals through which the gases must bubble are in use in some installations. Plates and bells are of copper.

descends, it gains in oxygen, while losing nitrogen, until there is collected at 5 liquid oxygen with only a trace of nitrogen.

For retail distribution to industrial users, the oxygen gas is delivered to a three-stage compressor which feeds it to seamless steel cylinders under a

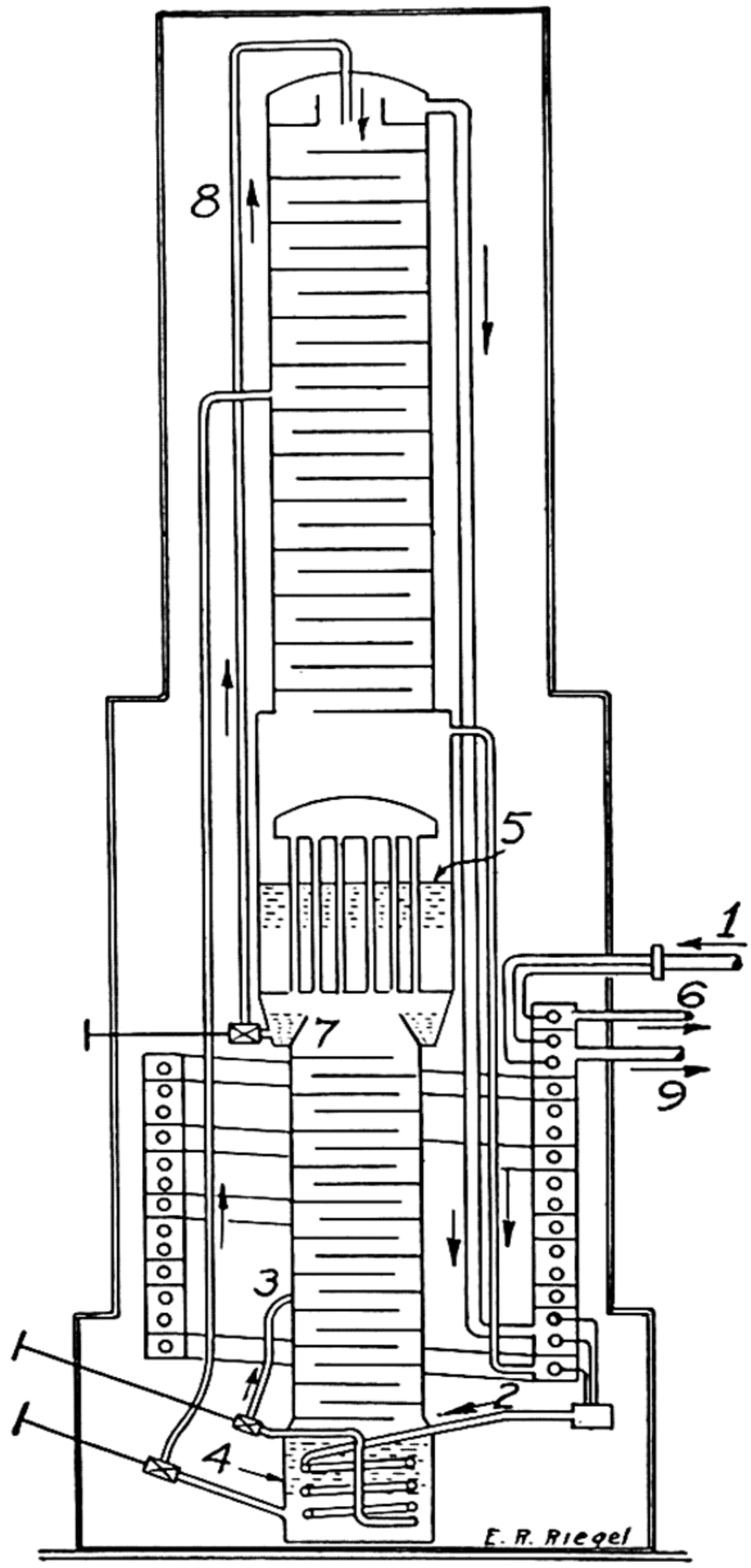


FIGURE 145.—Combined liquefier and separator with double column (Linde). The high-pressure air enters at 1, passes through exchanger coil 2, and is expanded, reaching the lower column at 3; liquid rich in oxygen collects at 4, while the gas rich in nitrogen reaches the top of the column, is liquefied there and collects at 7; from here it passes through a valve into 8 and to the top of the upper column; the liquid rich in oxygen passes from 4 to the middle of the upper column, loses its nitrogen on the way down, so that oxygen collects at 5; the oxygen passes out here, traverses the exchanger and leaves by 6; the nitrogen gas leaves at top of still, passes the exchanger and leaves at 9. Oxygen in the liquid form could be drawn off at 5, through an outlet (not shown) under the arrow; liquid nitrogen could be withdrawn at 7. Part of the liquefied nitrogen collects in 7; another part forms the reflux for the lower column.

pressure of 2000 pounds per square inch. In the compression, lubricating oil of the usual kind must be avoided. A steel container of 40-liter (water) capacity contains at that pressure and at 15° C. 6 cubic meters of free oxygen (212 cubic feet). It is delivered to the acetylene torch through a two-way diaphragm reducing valve, at a pressure slightly above atmospheric. Each cylinder is closed by an angle valve which at all times must be free from oil.

For large-scale users, the compressed gas containers become too numerous and involve too much container weight. It is primarily for the convenience of such users that the technique of transporting liquid oxygen was developed. Liquid oxygen at atmospheric pressure is transported in tank trucks and tank cars to its destination, where it may be stored. Liquid oxygen is carried in double-walled steel tanks, the space between the walls being filled with diatomaceous earth and then pumped out until the pressure is between 0.001 and 0.002 millimeter of mercury (practically a vacuum). From the tank car, the

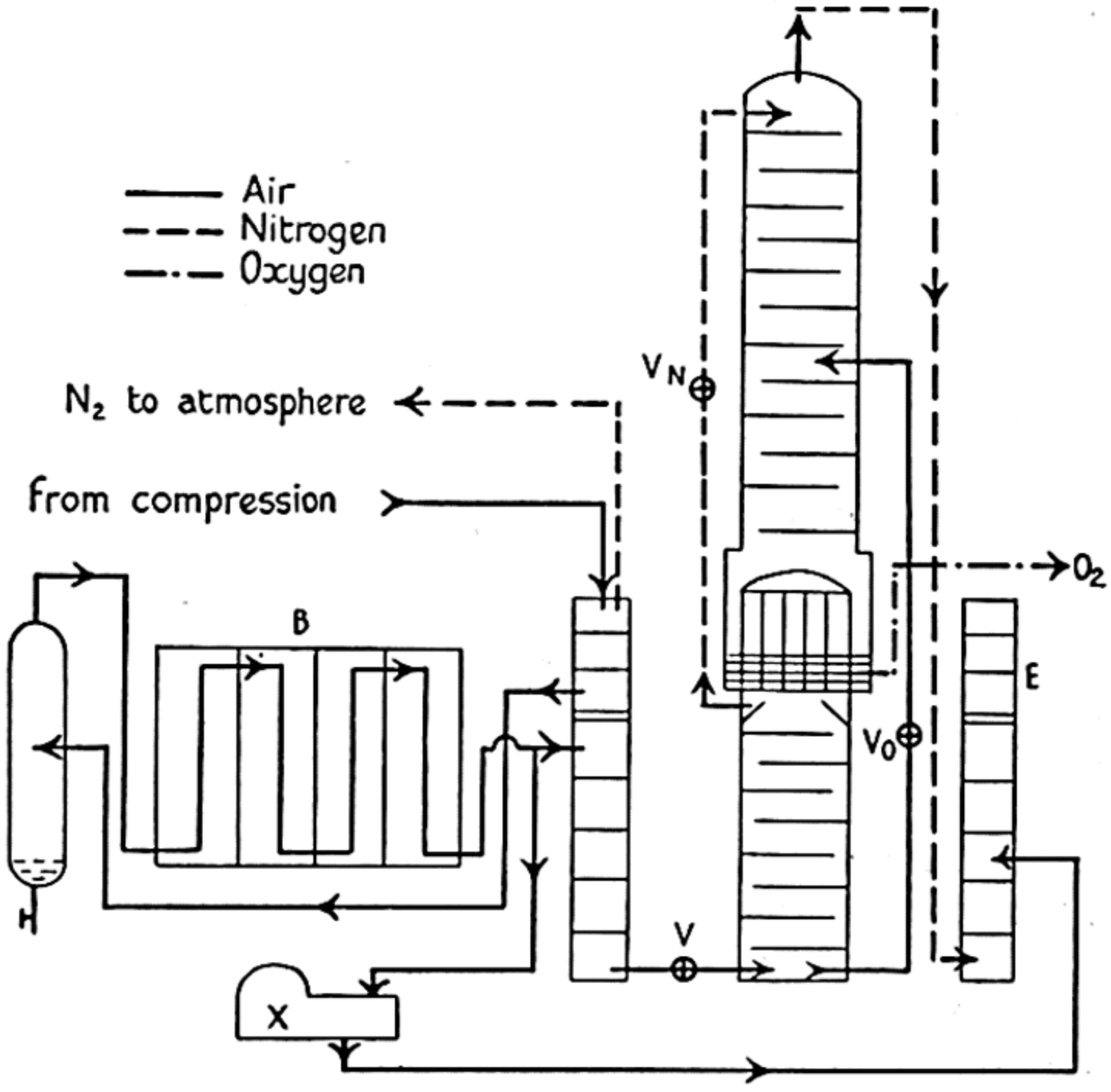


FIGURE 146.—The Heylandt cycle for liquid oxygen. B, the solid caustic soda battery; X, an expansion engine; V, expansion valve. (*From* Ruhemann, "The Separation of Gases.")

liquid oxygen is transferred to the storage tank by a pump. For use in the form of gas, the liquid is admitted to a vaporizer which transforms it to gas; the latter may be conveniently fed into a permanent gas line serving the shops. A slight compression would be sufficient.

It was this development which made it possible during World War II to deliver in a short time an abundance of oxygen from the manufacturing plant to a distant consuming point where it was needed. How badly it was needed will be apparent when it is recalled that the steel hulls of the Liberty ships were welded.

(2) The Heylandt cycle is designed for the production of liquid oxygen in large quantities. The compressed air is chemically freed from carbon dioxide and passed through the upper tier of the exchanger coils (see Figure 146) where most of its moisture is condensed and withdrawn; for final drying it is passed through a caustic soda battery (flakes and lumps)

at a pressure of 200 atmospheres. The gas stream is then divided; 40 per cent enters the lower tiers in the exchanger, where it reaches an expansion valve which allows it to expand to 4½ atmospheres' pressure, when part of it liquefies. Gas and liquid enter the bottom of the lower column. The remaining 60 per cent of the air at 200 atmospheres' pressure runs an expansion engine which discharges the gas at a pressure of 4½ atmospheres and −135° C. After cooling further by travel through separate coils in the heat exchanger, this stream also enters at the bottom of the column. The separator functions as explained previously. If gaseous oxygen is desired, the working pressure can be dropped to 60 atmospheres.

It will be noted that the Heylandt cycle makes use of both the Linde principle of cooling by expansion from a high to a low pressure without doing work (the Joule-Thomson effect), and the Claude principle of the conversion of energy (heat) into work by the expansion of a gas against a piston (or turbine).

The Rouget plant is designed for small-scale production of liquid oxygen, using the Claude principle. There are a number of other plants employing this principle for the production of larger amounts of liquid or gaseous oxygen, and for both oxygen and nitrogen.

In 1945, there were 179 plants in the United States making oxygen in all, and of these, 42 were Linde Air plants.

(3) There is considerable demand for low-cost oxygen for use in place of air to accelerate chemical or metallurgical processes and shorten the cycle time. Oxygen-enriched air could be made economically by mixing the low-cost oxygen with appropriate volumes of air. For the synthetic liquid fuels and chemicals process there is required a synthesis gas which is best made by means of low-cost oxygen.[14] About 16 years ago, several Linde-Fränkl low-cost oxygen plants were constructed in Germany. A 200-ton per day plant working on the Linde-Fränkl design is in successful operation in East Chicago, producing 90 per cent oxygen gas. During World War II the process was studied vigorously in the United States, in the course of which studies the reversing exchanger of Dr. S. C. Collins was developed, followed in turn by the reversing exchanger with unbalanced flow.[15] Low-cost oxygen is called "*tonnage oxygen*" in the United States. (See Figures 147 and 148.)

The low cost of tonnage oxygen has several bases. The purity is not high, for example, 90 to 95 per cent, so that the fractionating demands in the columns are much less stringent. The separating plant is located preferably across the road from the consuming plant, so that the gas may be transported and delivered a short distance away, under very moderate pressure, in pipes. The expense of compression and the investment in containers drop out altogether. Chemical purification of the air, with its consequent expenditures for chemicals is eliminated, completely in American plants equipped with reversing exchangers having unbalance, and almost completely

[14] "Tonnage oxygen," Charles R. Downs and J. Henry Rushton, *Chem. Eng. Progress*, 43, 12 (1947).

[15] "Reversing exchangers purify air for oxygen manufacture," S. C. Collins, *Chem. Eng.*, 53, 106 (December, 1946). "Air purification in the reversing exchanger," W. E. Lobo and G. T. Skaperdas, *Chem. Eng. Progress*, 43, 69 (1947). "Production of oxygen for industrial purposes," Walter E. Lobo, *Chem. Eng. Progress*, 43, 21 (1947).

in the Linde-Fränkl plants. The manufacturing cost is lowest for the very large plants (1000 tons a day). It might be said further that tonnage oxygen is the proper choice for a continuous supply of oxygen; for periodic supply on a major scale, liquid oxygen storage has advantages.

A further improvement is the reversing heat exchanger with unbalanced flow. The incoming air is under pressure (for example, 150 lbs/sq in.).

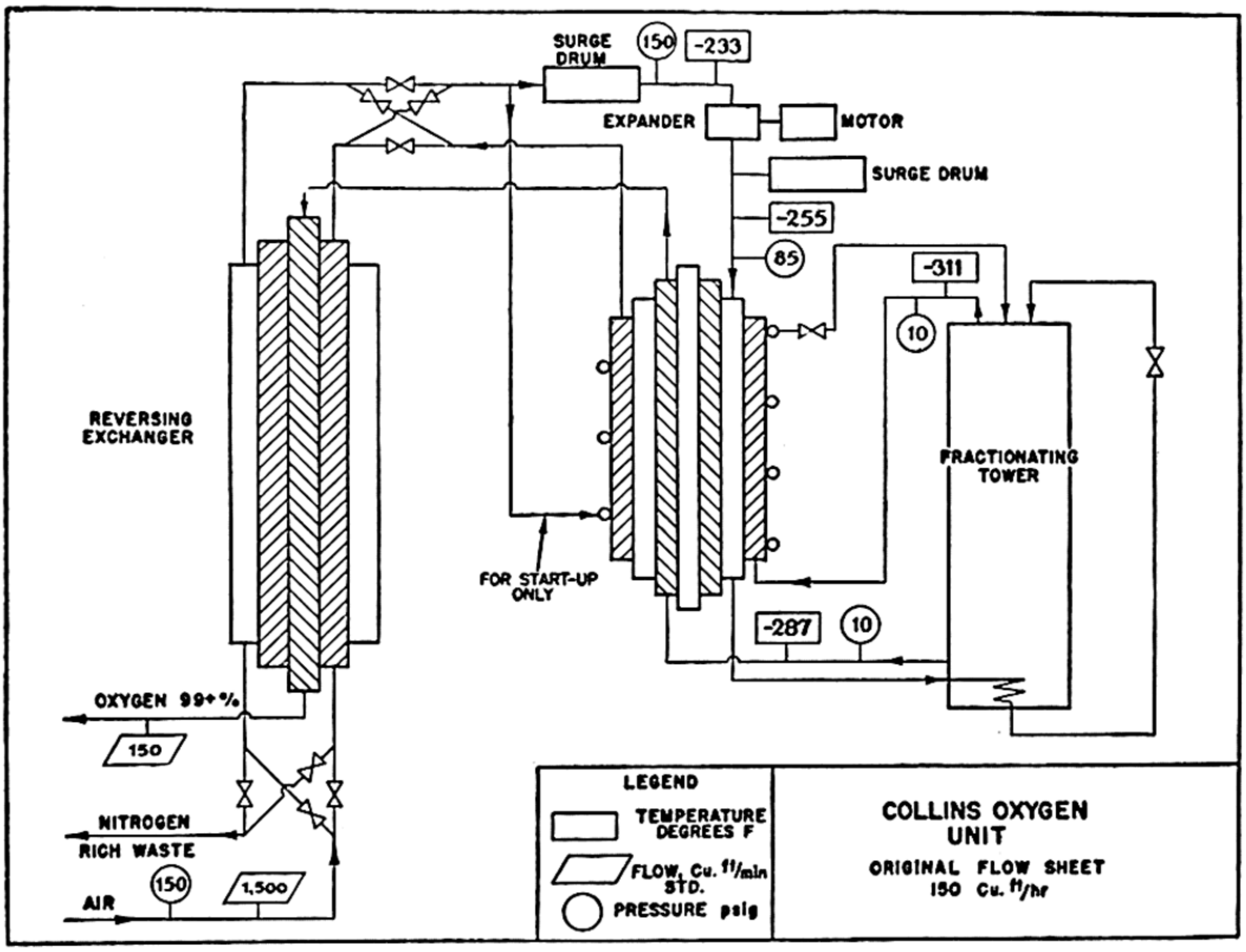


FIGURE 147.—Flowsheet of the original Collins oxygen unit showing the reversing exchanger. (*Chem. Eng. Progress*, 43, p. 62) (By permission).

It so happens that the specific heat of air increases (slightly) with pressure, so that the temperature difference between the two streams increases toward the cold end of the exchanger to values that endanger continuous operation. One scheme is to separate about 11 per cent of the cold nitrogen from the main mass and to circulate it in the exchanger, where it takes up some heat. The side stream then rejoins the main mass and both then enter the exchanger together (see Figure 148). The mass flow of the cold stream now exceeds the mass flow of the warm stream, and the temperature difference toward the cold end of the exchanger is decreased to below the critical values, and the exchanger can operate without interruption for long periods.

The cooled, purified air at −233° F. (−150° C.), enters a turbo-expander, for example, where it does work and drops in pressure from 150 to 85 lbs per sq in., while the temperature decreases to −255° F. (−160° C.). In a second heat exchanger operating at low temperatures, the air cools further, in exchange with cold gases coming from the fractionating tower. The

partly liquefied air successively reaches: a reboiler in the tower, where it gives up heat, a reduction valve, and the fractionating tower, which it enters at a pressure of 10 lbs per sq in. Nitrogen leaves the top of the tower at −311° F. (−190° C.), and oxygen near the base, at −287° F. (−176° C.).

The cycle just described is one of two in use in low-pressure oxygen plants. In the other, the stream of compressed air is divided, part of it going to the expander and the remainder to the column for processing. The former cycle requires a pressure of 150 lbs per sq in., in very small plants and about

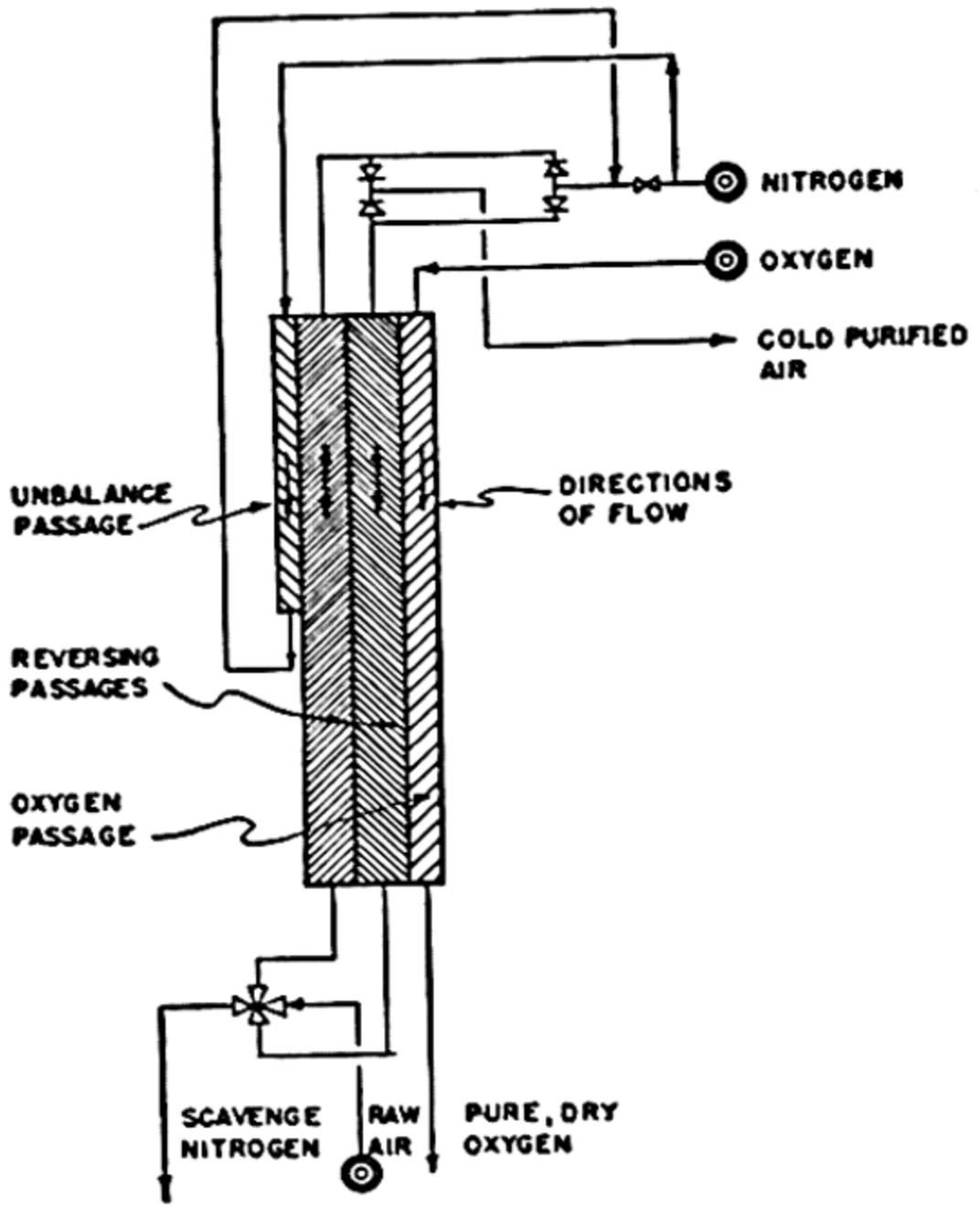


FIGURE 148.—The reversing exchanger with unbalance of mass flow. (*Chem. Eng. Progress*, 43, p. 70) (By permission).

90 lbs per sq in. in very large plants. The latter cycle requires about 85 lbs per sq in. for both large and small, but does not give quite as high a yield of oxygen. If the oxygen purity can be low, the pressures required are much lower with both cycles.

The heat exchangers may be ribbon-packed for maximum transfer of heat.[16] High-pressure systems working at 600 and 3000 lbs. pressure, respectively, have been described.[17] A new cycle in which reversals of the final clean-up heat exchangers will need to occur but once in 2 or 3 hours (instead of every 2 or 3 minutes) will work with a special heat exchanger; it will have thin copper fins bonded between brass plates, and an effective surface of 300 sq ft per cubic foot of exchanger volume.[18]

In the Linde-Fränkl system, the unbalance is secured in another way. Part of the incoming air is compressed to 200 atmospheres, precooled with ammonia, cooled with a special stream of cold nitrogen, and cooled further

[16] "The design of ribbon-packed exchangers for low-temperature air separation plants," P. R. Trumpler and B. F. Dodge, *Chem. Eng. Progress*, 43, 75 (1947).
[17] "Developments in oxygen production," J. Henry Rushton and Earl P. Stevenson, *Chem. Eng. Progress*, 43, 61 (1947).
[18] "Elliott oxygen system, how it works—description of cycle," B. H. Van Dyke, *Petroleum Refiner*, 27, 540 (1948).

by expansion in a valve, after which it is introduced into the upper column of the rectifier. In this way, the unbalance is provided by supplying a larger volume of nitrogen to cool a smaller volume of air than the normal one. There are still other methods.

In some of the very large plants, such as the 1000 tons a day plant previously mentioned, the exchangers may be replaced by recuperators, cylindrical shells packed with channels, or steel, or aluminum, and set up in pairs. In the pair marked "2" in Figure 149, nitrogen travels up the right hand recuperator, cooling it, while air travels down the left hand recuperator, cooling it, while air travels down the left hand recuperator, "picking up cold." In the right-hand vessel of the pair marked "3," oxygen travels upward, while air travels down in the vessel at the left, picking up the cold. The unbalance is produced as explained in the preceding paragraph; the amount of revert gases traversing the accumulator is greater in mass than the entering air.

Estimates of total plant costs and of operating charges are as follows:

TABLE 59.—*Estimates of costs of tonnage oxygen, 95% O_2.**

	For the production of 100 short tons per day	For the production of 1000 short tons per day
Estimated plant cost (1) ...	$1,000,000	$4,000,000
Operating cost per ton		
Steam (2)	$1.56	$1.46
Electricity (3)	0.11	0.11
Water (4)	0.35	0.30
Labor (5)	0.67	0.07
Maintenance (6)	0.72	0.29
Fixed charges (7)	3.61	1.44
Total operating cost per ton..	$7.02	$3.67

* Courtesy of Charles Raymond Downs, Chemical Engineer, 50 East 41 St., New York, under date of May 11th, 1948.

Notes:

(1) The plant cost is estimated as a turnkey installation, including engineering design, ordinary preparation of site, foundations, buildings, erection of equipment and installation of utilities within the confines of the plant. It does not include steam or power generating facilities because the unit costs assume that these utilities will be brought to the site. Obviously there is only one safe method for determining plant costs, namely, specific design for a given plant, taking into account all factors of locality and use of oxygen. Present estimates of plant costs have increased since the Tonnage Oxygen paper was published in January, 1947, to the approximate average figures estimated in the table. [*Chem. Eng. Progress*, 43, 13 (1947)].

(2) Steam is assumed to be used as the principal source of power, namely for gas compression, at $0.30 per 1000 lbs.

(3) Electricity will undoubtedly be used for driving small pumps and other accessories at $0.005 per kwh.

(4) Water for miscellaneous cooling purposes and for barometric condensation for steam turbines at $0.01 per 1000 gals.

(5) Operating labor at $67.00 per operating day for each plant.

(6) Maintenance at 2½% of the plant cost based upon 346 operating days per year.

(7) Fixed charges 12½% of the plant cost based upon 346 operating days per year. These allow for 10% depreciation and 2½% for taxes, insurance, etc.

Note should be made that the calculation of items (6) and (7) is based on 346 operating days per year. In other words the two plants are calculated to produce 34,600 tons and 346,000 tons of 95% oxygen per year respectively. It is believed that shut down time of 19 days per year is adequate for repairs. A smaller number of operating days per year would increase the operating cost per ton proportionately. It is obvious that the process using oxygen should be of the base-load type to attain low production costs.

No provision is made in the plant cost estimates for storage of oxygen or for power to compress it for processes requiring oxygen under pressure.

The cost of 95 per cent oxygen in a 1000 tons per day plant is much less than for a plant with smaller capacity; for the larger plant, 1000 cubic feet of 95 per cent oxygen in the gaseous state would cost about 15 cents, and twice as much for the smaller plant.

The purer gas, for welding purposes, is a different product. It may cost between $120 and $60 a ton (equivalent to $4.90 and $2.42 per 1000 cu ft), depending upon the quantity and shipping facilities. The familiar yellow portable steel cylinder containing 230 cubic feet of free gas is about $1 per 100 cubic feet, including rental of the cylinder.

(4) For the use of the Army during World War II there was required a portable low-pressure (150 lbs/sq in.) oxygen generator which would require

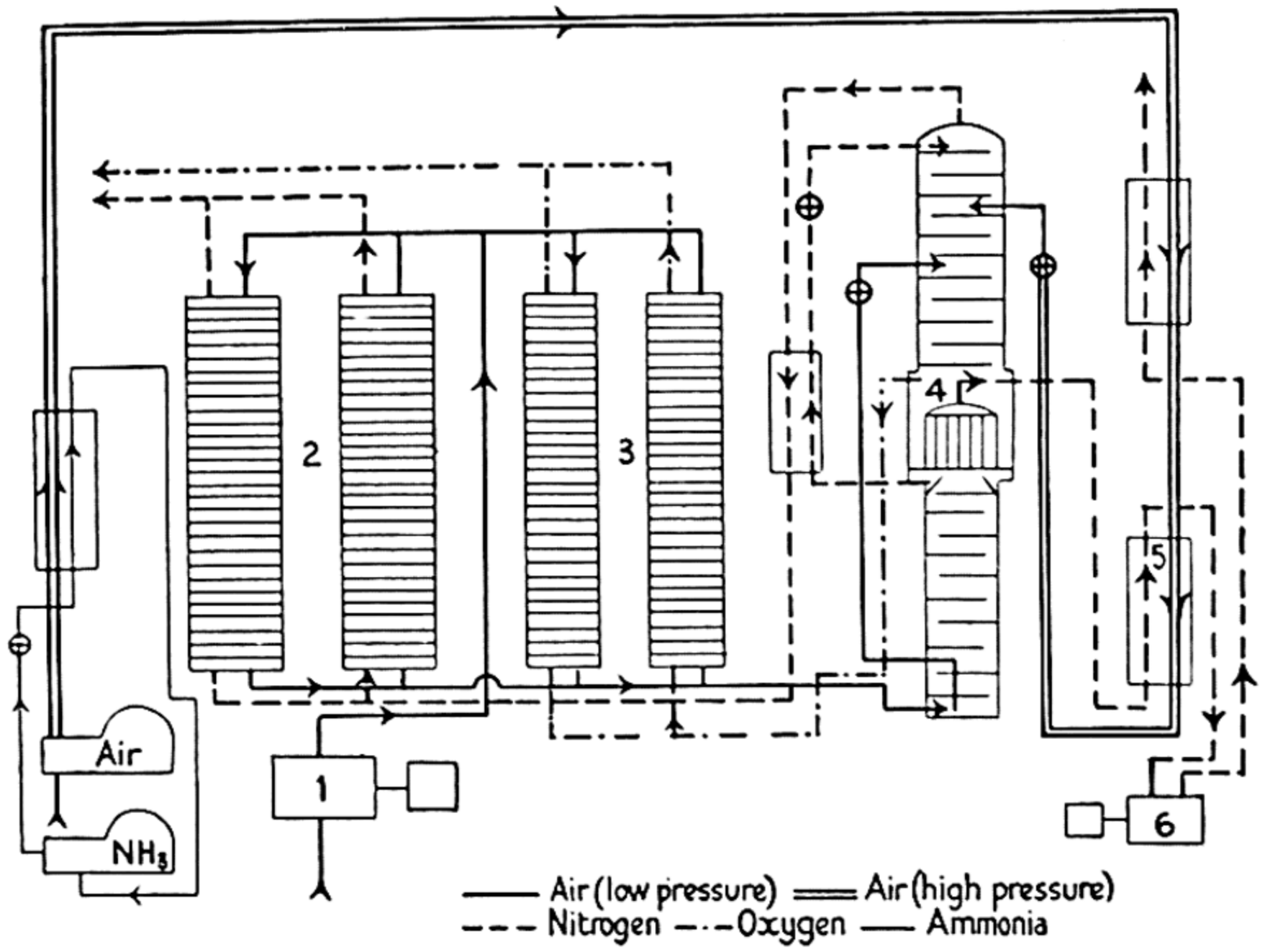


FIGURE 149.—Linde-Fränkl tonnage oxygen plant, with recuperators, working in pairs. (*See text.*) The air for unbalance is the double line, leading finally to the upper column of the rectifier. The main body of air is compressed at 1. (*From* Ruhemann, "The separation of gases.")

no chemicals for purifying the air. This task was solved successfully by the use of the reversing heat exchanger (see Figure 150). (Compare also temperatures and pressures in Figure 148.)

Nitrogen. The economical way to utilize liquefied air is to make use of both the oxygen and the nitrogen. This is not always possible. In general, oxygen plants liquefy air, save the oxygen and waste the nitrogen; while the manufacturer of cyanamide, for example, uses the nitrogen and is willing to waste the oxygen. There are increasing demands for nitrogen, however, as well as for oxygen. Nitrogen for the direct ammonia synthesis is not infrequently made from liquid air. Liquid nitrogen was used extensively as such for the shrink-fitting of parts for airplane engines and other assemblies during World War II, saving millions of man-hours; it is used in the same way now, though to a lesser extent. Liquid nitrogen is transported in its own special cars, similar in construction to the liquid oxygen cars but of larger capacities.

A major use of nitrogen as gas is in packaging and in bulk transportation of foods, which then remain fresh and attractive.

Argon. In a plant making nitrogen primarily, the argon will first accumulate with the oxygen; this impure oxygen is fed into a very tall column, entering about half-way up. There passes out at the top, through a dephlegmator cooled by liquid nitrogen, 50 per cent argon with nitrogen. This gas enters a second column with a similar dephlegmator at its top;

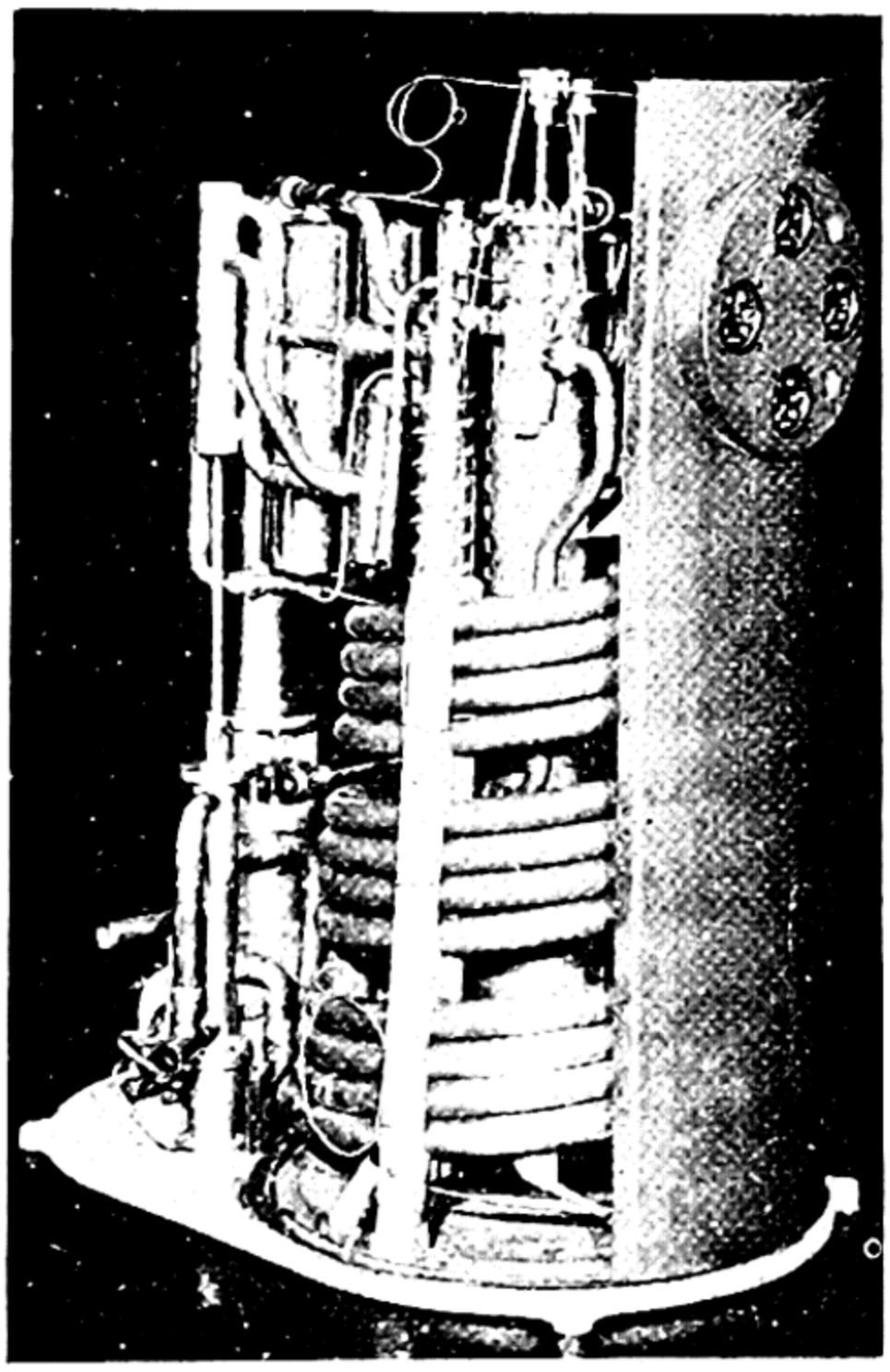


FIGURE 150.—A late model of the small aircraft low-pressure oxygen generator. Reversing valves at extreme left with expansion engine behind them. Rectifying column at center surrounded by reversing exchanger. The latter consists of a conical helix of four tubes in parallel, each tube containing three channels, one for oxygen, the other two alternately for compressed air and nitrogen. Compressor not shown. (Courtesy of Dr. S. C. Collins, Massachusetts Inst. of Technology, Cambridge, Mass.)

argon with an oxygen impurity is produced at the base, while the nitrogen passes out overhead.[19] The argon is freed of oxygen by passing it over heated copper. At atmospheric pressure, argon boils at −185° C., between oxygen and nitrogen. Considerable quantities of argon are being used for Heliarc welding. As originally devised, and as still practiced in certain operations, helium was the shielding gas in this process. The method is as follows: An arc is struck between a tungsten rod and the metal to be welded; a flow of helium gas is fed in through a sleeve forming a hemispherical envelope over the weld metal, protecting it from the air. The welding rod is fed in from the side. It has been found that argon may take the place of helium to advantage, for it is slower to escape, and a lesser volume of gas suffices. Argon is more abundant, and cheaper. Heliarc welding is recommended for welding magnesium, aluminum and stainless steel.

Argon is used to some extent to sweep traces of oxygen out of electric light bulbs just before sealing, and to fill gas-filled lamps.

[19] "Die fluessige Luft," by Kolbe, pages 338 to 343 (see read. ref.).

Neon Signs

Neon and several other rare gases in the atmosphere have been put to work in illuminated signs which allow novel and striking effects; the signs are spoken of collectively under the name "neon signs." These luminous signs consist of slender tubing, such as the chemist has long used in his laboratory, bent into the form of letters or figures. They contain a gas at low pressure (12 mm) through which an electric current of appropriate voltage is constantly passing. This voltage is 6000 to 12,000 volts, but the current quantity very small, 25 milliamperes; such current is obtained from the ordinary 120 volt A.C. lighting circuit connected to the primary, taking the high voltage current off the secondary winding of a transformer. Each sign is furnished by the manufacturer with a transformer which delivers the proper voltage. It is now customary for the sign company to sell service, rather than the sign and equipment, and to attend to the uninterrupted operation of the signs.

The voltage required depends, among other conditions, upon the particular gas or combination of gases used; this difference reflects the ionization potentials [20] of the single gases, listed in Table 60, with the color they produce, and the amount of the gases in the atmosphere.

Table 60.—*Properties of the rare gases of the atmosphere, and of mercury.*

	Ionization voltage 1st electron	Ionization voltage 2nd electron	Color	Parts per million in atmosphere
Helium	24.45	54.12	cream	5
Neon	21.48	40.9	red	15
Argon	15.70	27.82	bluish	9000
Krypton	13.90	26.4	light blue	1
Xenon	12.0	24.25	light blue	0.1
Mercury	10.39	19.0	green blue	....

Mercury forms part of the gas-vapor system in many tubes, because it carries the current easily, when the tube is "cold," for example, thanks to its low ionization voltage.

The tubing is of lead-potash glass 10 to 12 mm in diameter. The electrodes are copper, if no mercury is to be part of the tube, or iron, when mercury is used. The area of the electrode was considered an important feature at one time (Georges Claude). Leads sealed in the glass permit connection to outside lines. The electrodes are of sheet metal or woven wire. The tube is shaped over the flame, and its air pumped out through a sealed-in tee; next the current is passed for some time, with alternate exhaustion, in order to remove any trace of air. For a neon sign, neon gas from a one-liter supply flask is admitted by turning a glass-stopcock and reading a mercury gauge, until the pressure reads 12 mm.; this requires 2 or 3 seconds. The tube is then sealed off at a previously provided narrowed portion. If the cubical content of the sign is 50 cc., it receives $50 \times 12/760 = 0.8$ cc., so that a one-liter flask suffices for 1250 similar signs. The neon gas in colorless glass tubing gives an intense, very pleasing red. A small

[20] Ionization potential=potential for molecular distances required for formation of the ion.

amount of krypton may be mixed with the neon to lower the operating voltage. Mercury in clear-glass tubing gives a satisfactory blue; mercury and argon, a better blue. Mercury in amber glass produces green. Other colors are suggested in Table 60, still others by combination of colored tubes with certain gases. The smaller the diameter of the tube, the greater the voltage required, but the more luminous the column. The tube is continuous, for lengths totaling not over 10 or 12 feet; the parts not wanted are painted in black, and do not show.

Luminous signs may develop at an increasingly rapid rate if the hoped-for efficiency in the transformation of electrical energy into light is reached. Mazda lamps furnish 9 lumens per watt; neon tubes 10 lumens per watt. There is the further consideration that the human eye has a quite different sensitivity for the different colors; for example, 10 per cent of green will seem as intense as 90 per cent of red. George Claude has found that substituting xenon or krypton for argon in the Mazda lamp increases the light efficiency 33 per cent. Improvements in the electrodes for neon signs have been made; thus hollow tubes instead of rods have proved beneficial. Coating the electrode with easily ionized metallic salts [21] gives good results; thus a tube required 280 volts before coating the electrode and only 70 volts after coating it with cesium. The amount of light delivered by a tube depends upon the amperage, not upon the voltage.

The difference in ionization potentials may result in hiding certain gases in others, for example, 1 part of krypton in 3 million parts of helium is readily detected spectroscopically, but 1 part of helium in 2 parts of argon remains undetected.

The vapor of sodium is used for conducting the current and light production, in a double walled tube to prevent the condensation of the sodium, and with oxide electrodes to maintain a high current density; a special Jena or "Pyrex" Brand glass must be employed.[22]

Fluorescent Lamps. The Fluorescent Mazda lamps, also called Mazda F, have come into wide use. They are tubular lamps (100 watts: 60 inches long, $2\frac{1}{8}$ inches in diameter; 6 watts: 9 inches long, $\frac{5}{8}$ inch in diameter) consisting of a glass tube in which a drop of mercury has been placed, a small amount of argon or other gas, and an electrode at each end. The inner walls of the tube are coated with a fluorescent salt, such as zinc silicate, calcium tungstate, and cadmium borate. Under the action of the current, the mercury atoms give out a radiation (among others) in the ultraviolet, with wave lengths of 2537 Å; this invisible radiation activates the coating salt which now emits light over a broad range of wave lengths in the visible spectrum; for the salts mentioned, these are 4500-6200 (green), 3800-7000 (blue), and 4000-7200 Å (pink), respectively. Normal alternating current at 110 to 125 volts is used. The bulb wall temperature, in operation, is about 104° F. (40° C.).

[21] U. S. Patent 2,065,947, and 1,985,855.

[22] U. S. Patent 1,984,426, to Marcello Pirani; another patent to the same inventor, also for a sodium lamp, was 1,984,429.

Sulfur Dioxide

Of the more compressible gases, chlorine and ammonia are discussed elsewhere. Sulfur dioxide, SO_2, anhydrous, liquefied under a moderate pressure (2 to 3 atmospheres) at room temperature, is shipped in steel cylinders of 50 or 100 pounds capacity, in 1-ton containers, and in single-unit 15-ton car tanks. It is used from such cylinders and tanks in preparing hydroxylamine sulfate, which in turn serves in making dimethylglyoxime, the nickel reagent; for refrigeration, for bleaching, and, increasingly, in petroleum refining (Chapter 24). The boiling point is — 10° C.

The burner gas from sulfur (or pyrite), freed from dust, and cooled, is dissolved in water in two towers used in series; the solution from the second tower is elevated to the top of the first tower, where it meets the rich gas. Burner gas with 8 to 12 per cent sulfur dioxide yields a 1 per cent solution. In a third tower this solution is sprayed, at the top, and flows down, while steam is injected at the base of the tower; previously the 1 per cent liquor was heated in a closed coil laid in the spent liquor from the base of the still. The packing in all the towers may be coke, or special earthenware cylinders. The gas issuing from the third tower is cooled to remove most of its moisture, and is passed up a fourth tower down which concentrated sulfuric acid flows. The dried gas is compressed in a bronze pump to $2\frac{1}{2}$ atmospheres, which suffices to liquefy it.

Nitrous Oxide. Nitrous oxide, N_2O, is made by heating ammonium nitrate to 200° C., in small lots (50 pounds) in aluminum retorts. The gas is cooled in a condenser, washed in a solution of sodium dichromate to remove nitric oxide, in caustic to absorb nitric acid, and in water. Under a pressure of 100 atmospheres it liquefies, in small shipping cylinders, for instance; or it may be stored in a gas holder. The reaction is

$$NH_4NO_3 \rightarrow N_2O + 2H_2O.$$

Nitrous oxide is used as general anesthetic,[23] usually mixed with oxygen, and sometimes with ether vapor.

Carbon monoxide, CO, is a combustible gas, but carbon dioxide is not; it forms an essential part of water gas, discussed in Chapter 15. The monoxide may be liquefied with greater ease than hydrogen, and this fact was utilized by Claude in order to separate the two, as discussed in the first part of this chapter.[24] Carbon monoxide is poisonous. Carbon dioxide is discussed in Chapter 12.

Acetylene

Acetylene is an important industrial gas. The oxygen-acetylene flame produces the highest temperature of any combustible gas, hence its great value in welding and cutting of steel and other metals. Since its flame is white, brilliant and intense, it is used in lighthouses, light ships, and buoys.

[23] Chapter 30, *under* Pharmaceuticals.

[24] "The manufacture of hydrogen by partial liquefaction of water gas and coke oven gas," Georges Claude, *Ind. Eng. Chem.*, **14**, 1118 (1922).

Acetylene is generally made by the action of water on calcium carbide, a product of the electric furnace:

$$CaC_2 + 2H_2O \rightarrow \underset{\substack{\textit{acetylene}\\ \text{a gas}}}{C_2H_2} + \underset{\substack{\textit{hydrated lime}\\ \text{a by-product}}}{Ca(OH)_2}$$

One method of distribution is by means of portable steel tanks, containing a porous solid filler saturated with acetone, in which the acetylene is dissolved by pressure. Acetylene alone is not compressed to pressures higher than 2 atmospheres because of its tendency to decompose explosively; dissolved in acetone it may be under pressures of 10 or 15 atmospheres with safety. In order to fill the cylinders, the acetylene gas is dried over calcium chloride and compressed in a slow compressor (60 rpm). Several cylinders are connected at one time to the compressor and occasionally shut off to allow time for the solution in acetone. The capacity of the cylinder (40-liter volume) is about 13.5 to 14 pounds of acetylene, equivalent to about 200 cubic feet of free gas (1 pound of acetylene is equivalent to 14.5 cubic feet of gas). The Prest-O-Lite system of lighting depends for its bright flame (see Fig. 151) upon an acetylene cylinder. At one time, Prest-O-Lite was the standard lighting system in automobiles. The consumer may prefer to buy carbide and generate his own gas.

In the low-pressure generator, the pressure is below 6 pounds; in the "high-pressure" generators, it must not exceed 15 lbs per sq in. Carbide is fed a little at a time to a body of water. The volume of gas generated may be as low as 1 cubic foot an hour.

Large industrial establishments employ "dry generation" of the gas, in which a small continuous stream of water is added to the carbide; a mechanical agitator stirs the residual carbide and the dry lime formed, to prevent "hot spots." The ratio is about 1 pound of water to 1 pound of carbide, with the production of 0.31 pound of acetylene.

The gas may be stored in gas holders, or delivered under booster pressure to the consumer.

The third method of generation is the addition of drops of water to a stationary mass of carbide; this is the principle of the miner's lamp with open flame, used in mines free from explosive gases, such as rock salt, gypsum and certain coal mines.

There are two kinds of welding torches, high pressure and low pressure, and they differ in important details. Cutting torches differ from welding torches in the following way: in addition to the oxygen and acetylene conduits, which both torches have, the cutting torch receives a stream of oxygen around the flame; it is this oxygen which cuts the steel, by oxidizing it and forcing away the particles of oxide formed; the flame serves merely to attain the oxidizing temperature. The flame in each has an inner brilliant part, whose temperature is estimated at 3000° C.; in the welding torch this is surrounded by a larger envelope into which the air penetrates. The inner portion, which does the welding, is sometimes called the neutral part. (*Compare* Figure 151). The use of acetylene is not without danger; the directions and cautions of the manufacturer must be observed.

The oxyacetylene torch has many uses besides the welding and cutting of steel. It serves for metal cladding, in certain special circumstances; for steel conditioning, pressure welding, flame spinning, and flame hardening. In the shaping of synthetic sapphire and ruby (hexagonal crystals of alumina) the torch is in constant application. The synthetic ruby, for example, is obtainable in the form of slim rods and boules (balls); the rods when heated in the torch may be bent, in the form of a thread guide, let us say, which is a complete loop. At the same time, the material acquires a flame finish of extreme smoothness. Ruby in rod form is made into precision gauges. It is made into extrusion dies, phonograph needles, and knife edges on balances.

Other cheaper sources of acetylene are being actively sought; high-temperature cracking of natural gasoline with recirculated ethylene to produce acetylene and hydrogen promises a yield of acetylene of better than 50 per

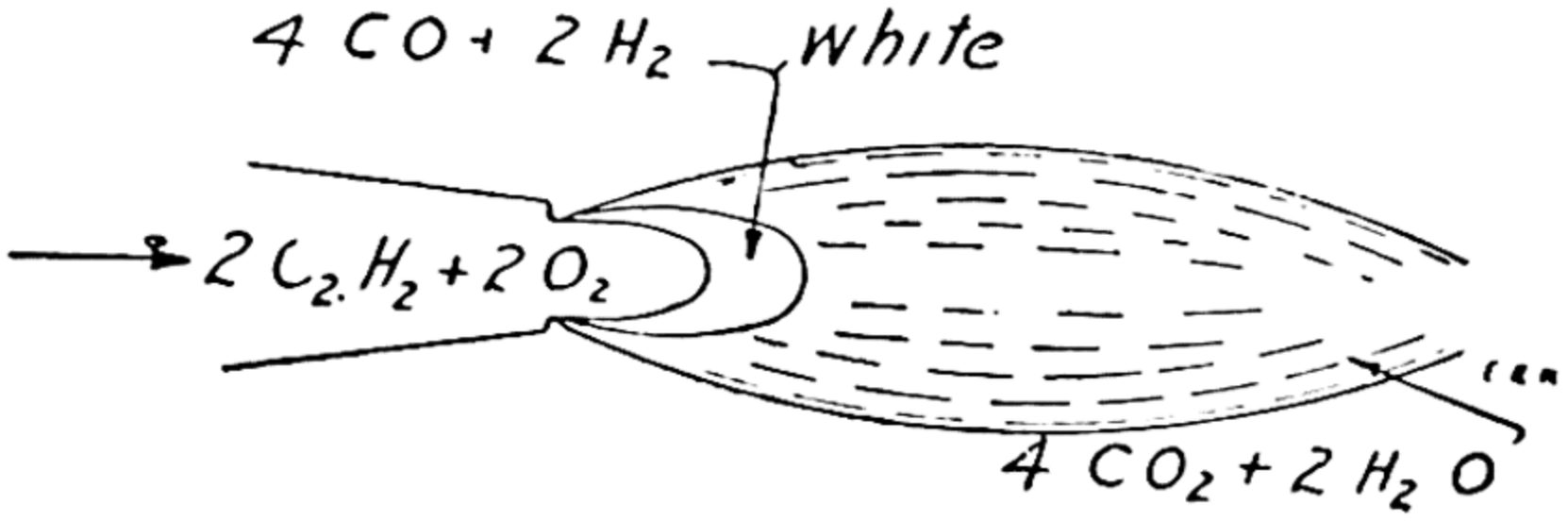


FIGURE 151.—The oxygen acetylene flame (*after Vogel*).

cent (on the butane charged). An arc cracking process of coal hydrocarbon gases, containing, for example, 80 per cent methane-ethane, developed in Germany in recent years, gives a 15 to 16 per cent conversion.[25] The reacted gas is purified by removal of carbon black, then cooled, washed with oil, with water to remove hydrogen cyanide, and passed over hydrated iron oxide mass to remove sulfur. It is then compressed to 19 atmospheres and scrubbed with water, which dissolves the acetylene. A four-stage flashing gives pure acetylene in the last three. The main method in Germany itself is the carbide method.

Acetylene undergoes a number of reactions which are the bases of several large industries. Acetylene as a chemical substance is presented in Chapter 25. In the recent advances made in Germany by Dr. Reppe, processes which required pressures greater than a few pounds were required; many required 30 atmospheres. The generally accepted limit in the United States has been 1 atmosphere. It was essential to discard the conception that acetylene is a dangerous substance at even slightly elevated pressure and temperature, and to study instead under what conditions higher pressures might safely be applied. Many such studies had been made by chemists everywhere and certain points settled, but never as systematically as by Dr. Reppe. Admixing an inert gas such as nitrogen is an effective way to desensitize acetylene. The Reppe acetylene chemistry will be described in Chapter 25 also.

[25] *Chem. Met. Eng.*, 49, no. 7, 78-83 (1942).

Unionmelt is an apparatus and process for high-speed, automatic welding with an electric arc. Welding wire on a reel and flux from a hopper are fed in at the proper rate, and the whole assembly of electric torch, reel, hopper and small motor move as fast as the weld is formed. Long, formerly tedious, straight-line welds are made in this way.

Welding by the Atomic Hydrogen Flame

A welding torch has been developed in which atomic hydrogen, produced by passing hydrogen through an electric arc produced at the torch, furnishes the heat for welding as it combines to form molecular hydrogen. The temperature is as high or higher than that of the electric furnace; it is estimated as between 4000° and 5000° C., so that materials hitherto infusible may be fused. The weld produced may be worked as readily as the original sheet. This flame has the additional advantage that it is non-oxidizing and non-carbonating.[26]

Production. Tables 61 and 62 give the production of compressed gases. Vast quantities of these gases processed at once are not reported.

Table 61.—*Production of compressed gases.**

Hydrogen, for 1946, annual	17,605,000,000 cubic feet in 88 plants
Oxygen, for 1946, annual	10,868,000,000 cubic feet in 222 plants
Acetylene, 1945, nine months	
for use in chemical synthesis	2,733,567,000 cubic feet
for commercial purposes	1,116,248,000 cubic feet
Nitrous oxide, 1945, nine months	119,154,000 gallons
Carbon dioxide, 1946, annual	
liquid and gas	217,241,000 pounds in 57 plants
solid (dry ice), annual	644,699,000 pounds in 48 plants

* "Facts for Industry," Bureau of the Census.

An earlier set of figures, for a pre-war year, included prices.

Table 62.—*Production of compressed gases.**

	Cubic feet	Value per 1000 cubic feet
Hydrogen	1,124,168,000	$ 1.38
Oxygen		
by liquefaction	4,452,209,000	
by electrolysis	109,759,000	5.28
Acetylene	1,274,164,000	13.00
Nitrous oxide	95,577,000	9.00
	Pounds	**Value per pound**
Carbon dioxide, liquid	102,208,118,000	.04
Dry Ice	356,893,516,000	.0155
Ammonia, anhydrous	227,219,049	.0374

* Bureau of the Census.

Other Patents

U. S. Patent 1,850,529, extraction of helium from natural gas, wherein its percentage is comparatively small; 1,881,115 and -6, helium from gaseous mixtures which have boiling points above the critical temperature of helium; 1,772,202, extraction of krypton and xenon from liquid oxygen, by increasing the concentration, then passing through an absorbent for krypton and xenon; 1,892,186, production of argon and neon

[26] "Flames of atomic hydrogen," Irving Langmuir, *Ind. Eng. Chem.*, 19, 667 (1927); or, *General Electric Review*, 29, 153 and 160 (1926).

as by-products in the synthesis of ammonia from atmospheric nitrogen; 1,872,741, production of dry acetylene from calcium carbide and effecting complete hydration of the carbide; 1,794,004, production of acetylene and hydrogen in the electric arc; on isolation of argon, Brit. Patents 218,266 and 226,783 (1924) and U. S. Patent 1,420,802.

Knowles' patents, on electrolysis of water: 1,067,822, apparatus for purifying electrolytic gases by combustion; 1,566,543, electrolytic cell, automatic control of liquid level in electrolytic cell and washing of the gases evolved; 1,485,461, electrolytic cell for production of H_2 and O_2 by electrolysis of water; 1,866,472, electrolytic apparatus for washing gases evolved from a cell by causing them to bubble through water; 1,856,218, electrolytic apparatus using thicker sleeve around the electrode on the sides not facing the opposite electrode in order to maintain a high purity gas; 1,856,393, temperature controlling system for electrolyte in electrolytic cells; 1,767,292, gas washer for electrolytic apparatus by bubbling gases through chambers containing the washing fluid; 1,767,375, washing gases by bubbling them through chambers containing the washing fluid; 1,821,018, electrolytic apparatus for electrolysis of liquids for production of gases. 2,236,534, on thermal cracking of natural gasoline to produce acetylene; 2,380,417, on making industrial oxygen.

Problems

1. In the steam-iron process for hydrogen, the retorts as given in the text produce 3500 cu. ft. per hour. Over the day, how many hours are all the retorts in actual operation making hydrogen? Disregard purging period. If 3 times the amount of necessary steam is taken, what is its weight?

2. In the installation of 306 Knowles' cells given in the text, let the current efficiency be 100 per cent, and let the operating voltage be 2. What is the energy efficiency? Compare Chapters 5 and 18. For the production of hydrogen gas as specified, how much distilled water will be required?

3. Let the "parts per million" for the rare gases in the atmosphere represent volumes. How many cu. ft. of air will be required in order to prepare 1 liter of each of the rare gases? The first operation for liquid oxygen has a 90 per cent yield; assume that its rare gas content is the same as in the original air. The recovery on from there may be taken as 80 per cent.

4. An acetylene generator receives a charge of 250 pounds of calcium carbide, 75 per cent CaC_2. What is the volume of acetylene gas which may be generated, measured at ordinary temperature and pressure?

Reading References

"Hydrogenation in practice and theory and the manufacture of hydrogen," E. F. Armstrong, *Trans. Inst. Chem. Eng. (London)*, 9, 13-9157 (1931).

"The manufacture of hydrogen by the partial liquefaction of water gas and coke-oven gas," Georges Claude, *Ind. Eng. Chem.*, 14, 1118 (1922).

"Industrial hydrogen," Hugh S. Taylor, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.) 1921.

"Industrial gases," H. C. Greenwood, New York, D. Van Nostrand Co., 1919.

"The commercial production of pure hydrogen from hydrocarbons and steam," R. M. Reed, *Trans. Am. Inst. Chem. Eng.*, 41, 453 (1945).

"Present-day hydrogen manufacturing processes," R. M. Reed, *Trans. Am. Inst. Chem. Eng.*, 42, 379 (1946); also *Petroleum Refiner*, 25, 99 (1946).

"Properties and uses of helium," W. E. Snyder and R. R. Bottoms, *Ind. Eng. Chem.*, 22, 1189 (1930).

"The government's new helium plant at Amarillo, Texas," *Chem. Met. Eng.*, 37, 550 (1930).

"The production and uses of helium gas," R. R. Bottoms, *Aeronautical Eng.*, 107, (1929).

"Turbo-expanders," Judson E. Swearingen, *Trans. Am. Inst. Chem. Eng.*, 43, 85-90 (1947).

"Linde Air holds editorial meeting on oxygen," *Chem. Eng. Progress*, 43, 16 (1947).

"Production and use of gaseous oxygen, methods and economics," *Ind. Chemist,* 24, 153 (1948).

"The separation of gases," M. Ruhemann, International series of monographs of Physics, Oxford, Great Britain, University Press, 1945.

"Production and use of gaseous oxygen," Conference report on recent developments, *Ind. Chemist,* 26, 153 (1948).

"Der Sauerstoff," M. Laschin, Halle a.S., Germany, Carl Marbold Verlagsbuchhandlung, 1924 (100 pages).

"Fluessige Luft," Ludwig Kolbe Leipzig, Johann A. Barth, 1920. This is the German translation, enlarged, of "Air Liquide, Oxygéne, Azote," by Georges Claude, Paris.

"Liquid air fractionation," J. G. Aston, W. E. Lobo and Brymer Williams, *Ind. Eng. Chem.,* 39, 718 (1947); "Rectification of liquid air in a packed column," John A. Weedman and B. F. Dodge, *Ind. Eng. Chem.,* 39, 732 (1947).

"Liquid oxygen as an explosive," F. W. O'Neil and H. Van Fleet, *Am. Inst. Min. Met. Eng.,* 74, 690-731 (1926).

"Traces from tons," F. J. Metzger, *Ind. Eng. Chem.,* 27, 112 (1935).

"Acetylene," G. R. Webster, R. L. Hasche, Encyclopedia of Chem. Technology, 1, 101-123 (1947), publ. by Interscience Encyclopedia Inc., 215 Fourth Avenue, New York 3, N. Y.

"The Chemistry of Acetylene," Julius A. Nieuwland and Richard R. Vogt, A.C.S. Monograph 99, New York, Reinhold Publ. Corp., 1945.

"Acetylene from petroleum gases," Peter W. Sherwood, *Petr. Ref.,* 27, 573 (1948).

"Acetylene industry in wartime Germany," R. Leonard Hasche, *Chem. Met. Eng.,* 52, 116 (1945).

A table of compressed gases and gas regulators, containing 69 items, each available in several size cylinders, with much pertinent information, is published by The Matheson Company, East Rutherford, N. J., P. O. Box 85.

"Tonnage Oxygen for chemical industry," J. T. Hugill, *Can. Chem. Process Ind.,* Dec. 1947, p. 1115.

"Acetylene and Carbon Monoxide Chemistry," J. Copenhaver and M. H. Bigelow, New York, Reinhold Pub. Corp., 1949.

A number of chemical industries depend upon the existence of minute plant organisms, so small that they are visible only under a high-power microscope; they are therefore called microorganisms. Under the proper conditions, they grow at enormous speed; they apparently have the power to consume one substance and to produce another, and it is this function which makes them valuable. In these industries, the chemist joins hands with the bacteriologist.

Chapter 20

Processes Based on the Activity of Yeasts and Bacteria

From time immemorial, one of the processes which depends upon the existence and growth of microorganisms has been practiced, namely, that of alcoholic fermentation of grape juice and fruit juices. Its exact nature remained a mystery until Louis Pasteur discovered, isolated, and classified the several kinds of organisms. He succeeded in demonstrating that fermentation and bacterial disturbances in general are not due to spontaneously generated plant organisms, but to organisms which already exist elsewhere and which are carried in by air currents,[1] on the skin of the fruit, or in other ways. At the same time, the nature of the festering of wounds became clear; as a result, the modern science of antiseptic treatment was born.

The transformation of certain sugars (the monosaccharides, such as glucose and fructose) into alcohol is brought about by yeast; carbon dioxide is evolved profusely at the same time, so that the liquid seems to boil.[2] The formation of lactic acid is due to a bacterium. The place of these organisms in the complete group will be clearer from some general considerations.

Yeasts, bacteria, and molds are fungi, vegetable growths. Yeasts multiply by budding, with or without spore formation; bacteria multiply by division or fission, in rare cases by spores. Yeasts show a definite nucleus under the microscope, whereas bacteria do not. Yeasts are commonly egg-shaped, and about 0.01 mm. in diameter; bacteria are long or short rods,[3] comma-shaped, and in general smaller than the yeasts (about one-tenth the size of yeasts). Bacteria and yeasts differ from molds in that the former are unicellular, while the latter are multicellular. Molds multiply by sporulation. Protozoa are the lowest form of animal life; they are one-celled, and are found in ditch water (amoeba).

The yeast cell contains complex organic substances called enzymes, whose characteristic is that they catalyze a chemical reaction; the reaction they catalyze is the same as the one the cell as a whole catalyzes. As a rule, yeast contains a number of different kinds of enzymes. In industrial operations, the enzyme is not isolated; the cell is cultivated and used. For growth, the alcoholic ferment requires sugars, a small amount of mineral salts, phosphates, and nitrogenous matter. The effort of the manufacturer is not to grow yeast, for 1 gram of pure yeast requires 1 gram of sugar,

[1] Pasteur had to ascend the Alps many hundreds of feet above human habitation before he could find air which would not contaminate his test solution (veal broth).

[2] Hence the name fermentation, from the Latin word *fervere*, to boil.

[3] The long rods are bacilli; the short ones, bacteria proper.

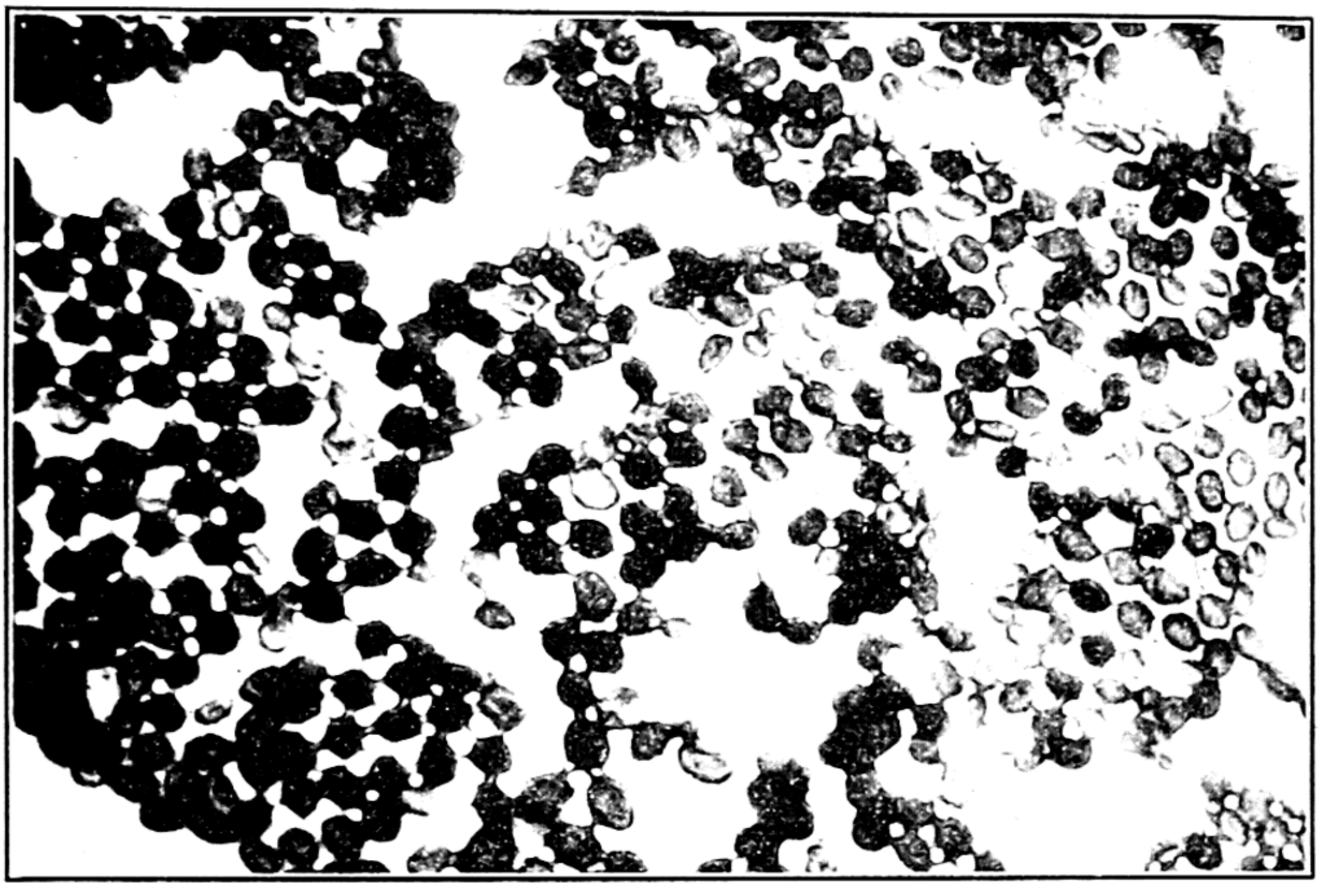


FIGURE 152.—Yeast cells, magnified 300 times. The light cells are the disintegrating ones; the dark cells the growing ones. The inter-connection between mother and daughter cells is shown in the lower left; in several places, a cell with bud formation is visible.

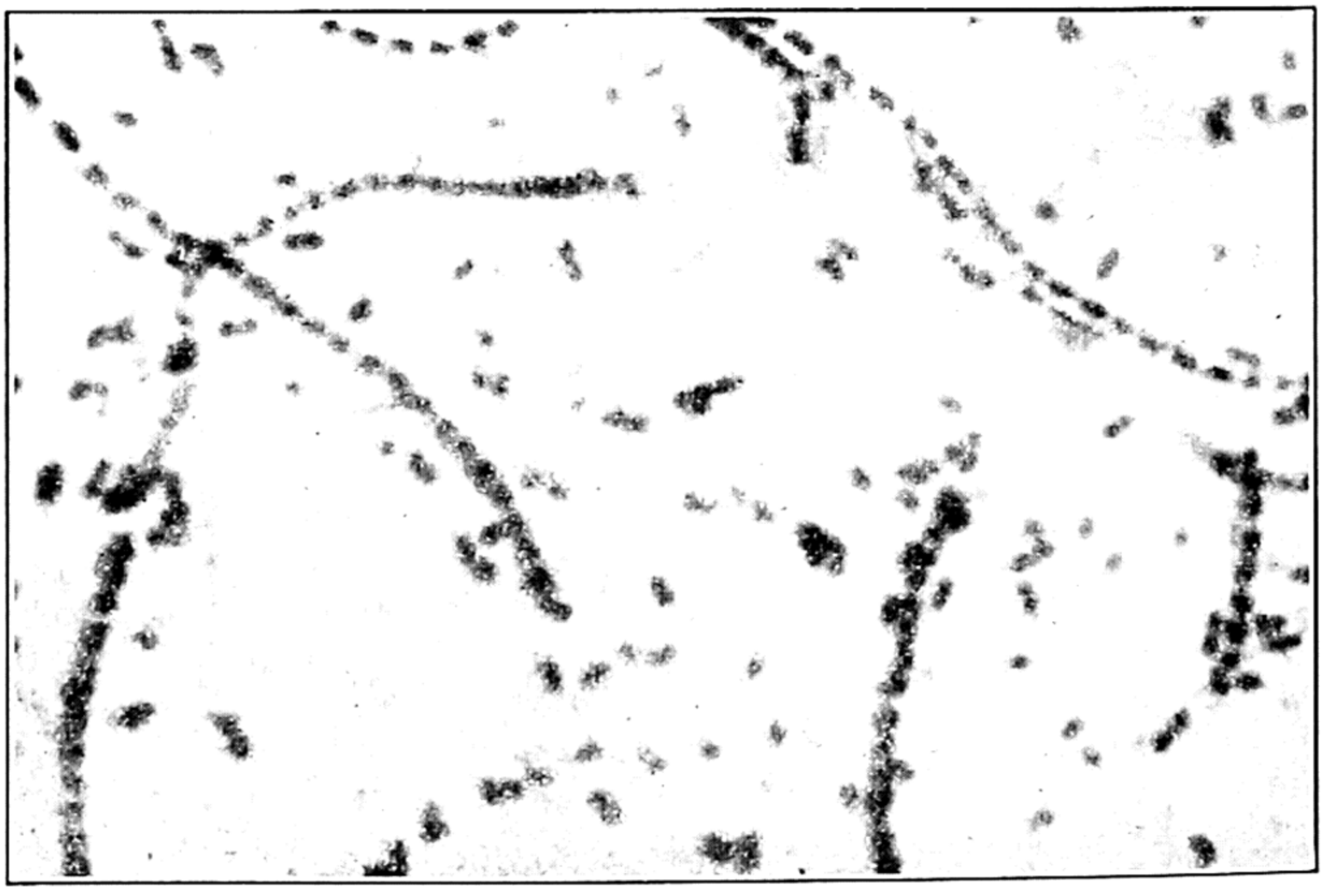


FIGURE 153.—Bacterium lactis acidi, used for the production of buttermilk, magnified 1800 times.

and hence there would be no production of alcohol, but rather to produce just enough yeast to catalyze the alcohol-forming reaction. Some growth takes place, but most of the conversion is due to the action of the cells formed.

Yeasts and bacteria grow best and work best at definite temperatures, which vary with the several organisms but lie not far from room temperature, perhaps between 5° and 40° C.; 60° is fatal to most of them. In general the working range for bacteria is narrower than for yeasts. These microscopic plants are carried about by every gust of wind, so that it is difficult to keep any one batch of liquid free from contamination. In order to control the action, all organisms already in the material are destroyed by a preliminary heating, called sterilization; after cooling, a pure strain of the desired organism, grown under protection (aseptic conditions), is introduced; this is called inoculation, or seeding. Not only the temperature, but the acidity has an effect on the activity (and growth) of the organisms; alcoholic ferments work well in an acid medium, while most of the bacteria are inactive; on the other hand, too high a concentration of alcohol will destroy the yeast itself. In order to grow, yeast requires air; it causes fermentation best out of contact with air.

Industrial Alcohol

Fruit juices are fermented and distilled to concentrate the alcohol formed, for the production of potable spirits whose value lies largely in the flavor characteristic of the particular fruit used; the finished liquor purposely betrays its origin. It is different with industrial alcohol, for this must be as nearly chemically pure as possible, and must bear no marks of the original material. Industrial alcohol is ethyl alcohol, 95 per cent. Ethanol is another name for ethyl alcohol. The sources of industrial alcohol must be cheap, otherwise the uses will be limited; preferably by-products of other industries which can be worked up into alcohol are sought.

A distinction must be made at once between (a) fermentation processes, and (b) synthetic processes which involve no organism or enzyme, but depend exclusively on chemical reactions. The distinction is made merely for clarity. In the United States and in England, the chief raw materials for (a) are cane-sugar molasses and beet-sugar molasses; in France, sugar beets and sugar-beet molasses; in Germany, at least before 1939, potatoes. Any starchy material may be used, such as corn and certain other grains, although these are generally more valuable for food. The liquor from the wood-pulp digester has been made into a source of alcohol,[4] and wood and sawdust have been used in experimental plants (Chapter 16).

The processes in (b) are represented by the catalytic hydration of ethylene; the ethyl sulfate process, itself based on ethylene; and the synthetic liquid fuels processes, which aim at gasoline but produce oxygenated compounds as by-products, of which one is ethyl alcohol. Such synthetic processes do not strictly belong to this chapter, but the economic relation forces their consideration. The industry was originally dominated by the

[4] "Alcohol from sulfite waste liquor," E. O. Ericsson, *Chem. Eng. Progress*, 43, 165 (1947).

fermentation processes, until the product made from ethylene, lower in price, became its rival. The synthetic liquid fuel processes are expected to produce ethyl alcohol for even less.

Industrial alcohol is itself a raw material for chemicals; it is also a solvent. It is not subject to the Federal alcohol tax ($9 per gallon, 100 proof). In order to prevent the diversion of industrial alcohol to potable uses, it is "denatured" by the addition of some material which cannot be separated by any physical or chemical process and which renders the alcohol so treated unfit for use as a beverage. A large number of different formulas are authorized by the Government, so that the industrial user may select the particular formula which will have least effect upon his particular process. Under the supervision of Federal inspectors, chemical processes which require pure industrial ethyl alcohol may be operated.

For molasses, the process is essentially a fermentation, followed by distillation. For corn and other grains, potatoes, and similar starch-containing raw materials, the starch must first be liberated and solubilized and then converted into sugar; the latter is then fermented, and the fermented liquor distilled for its alcohol.

Alcohol from Molasses. Molasses is the final mother syrup in the crystallization of sucrose or table sugar; 15 to 20 per cent of the sugar in the sugar-cane juice, or in the sugar beet, cannot be crystallized, because the accumulated non-sugars interfere with crystallization. Cane-sugar molasses differs somewhat from beet-sugar molasses, as shown below.[5]

TABLE 63.—*Analysis of typical cane and beet molasses.*

	Cane molasses	Beet molasses
	Per cent	
Water	20	20
Sucrose	30	50
Raffinose	0	present
Invert sugar	32	trace
Ash	6	10
Organic non-sugars	12	20

Sucrose is a disaccharide, $C_{12}H_{22}O_{11}$; in the presence of water, it is converted by invertase, an enzyme present in yeast, into two molecules of monosaccharides:

$$\underset{\textit{sucrose (d)}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\textit{d-glucose}}{C_6H_{12}O_6} + \underset{\textit{l-fructose}}{C_6H_{12}O_6}$$

The newly formed monosaccharides, glucose and fructose, as well as the invert sugar present in the molasses, are attacked by the enzyme zymase, the most important enzyme in yeast, and change into alcohol and carbon dioxide. Invert sugar consists of equal parts of *d*-glucose and *l*-fructose.

Cane-sugar molasses is received in alcohol plants along the Atlantic seaboard in the form of a thick dark syrup, transported in tankboats holding from 1 to 2 million gallons. Inland, molasses is transported by railroad tankcars. At the alcohol plant, the molasses is diluted with enough water to produce a solution or "mash" containing about 10 per cent of sugar, and

[5] The chemist distinguishes many kinds of sugars; sucrose, glucose, and fructose are discussed in this section; raffinose is a tri-saccharide, with C_{18}; *see* Chapter 23.

made slightly acid by the addition of sulfuric acid. The acidity retards bacterial action, and promotes a vigorous growth of the yeast. The mash is brought to a temperature of 70° F. (21° C.), pumped into the fermenter, and a prepared yeast culture added. The yeast suspension is about 5 per cent of the volume of the mash. Considerable heat is evolved during fermentation, causing the temperature of the mash to rise. By means of cooling coils, the temperature is kept below 100° F. (37.8° C.).

In about three hours after the addition of the yeast, the evolution of carbon dioxide may be observed. The action gradually increases, until at the end of 24 hours the entire mash appears to boil. The yeast mash contains and furnishes many enzymes, among others invertase, maltase and zymase. In the early stages of fermentation the yeast grows, the enzyme invertase converts the sucrose to the monosaccharides; soon, the zymase proceeds rapidly to convert the glucose and fructose into alcohol and carbon dioxide. The principal reaction during fermentation is:

$$\underset{\substack{l\text{-fructose or}\\ d\text{-glucose}}}{C_6H_{12}O_6} \longrightarrow 2C_2H_5OH + 2CO_2$$

Other products formed are fusel oil, higher alcohols (of which isoamyl alcohol is the principal one), glycerin,[6] and a small amount of organic acids. The fermenters are generally covered, so that the carbon dioxide may be piped away, and either wasted or recovered.[7] The time required for complete fermentation may be two days.

The main product of the fermentation is a weak alcohol, the "beer," which is distilled. The more concentrated distillate is then rectified (see later). The final product is 95 per cent ethyl alcohol. The yield is about 0.4 gallon (U. S.) per gallon of molasses, analyzing as shown in Table 63, and this represents about 90 per cent of the sugar converted to alcohol. The loss is due partly to the escape of vapors in the gas.[8] The residue from the distillation is a more or less clear liquid which may be concentrated to 32° Bé.; the thick liquid resulting supports its own combustion, and is burned in special furnaces for the potassium salts which it contains. The primary purpose of the operation is to dispose of the enormous amount of waste liquor. The yeast remains in the liquor and is destroyed. The species of yeast best suited is taken from the surface of the sugar cane; pure cultures are grown from it and used in the process.

Alcohol from Corn. A raw material in high favor in the United States is corn, because of the bountiful crops generally available. In past years, the price has been reasonable, especially for slightly lower grades. The corn is unloaded at the plant by suction, which simultaneously removes dust and light materials (impurities); it is screened, and passed over magnetic separators. The clean grains are fed to mills which break the kernel and produce a meal of practically uniform granulation. On storing the meal, heat may develop and damage it; also, it may become contaminated with foreign organisms. Preferably, therefore, storage is avoided altogether, and the meal

[6] Chapter 32.
[7] Chapter 12.
[8] In the installations with carbon dioxide recovery, this alcohol is saved.

is fed directly into the cooking system. For this purpose, the meal is mixed with water to a slurry which is precooked (2 to 3 minutes) at 145-155° F. Thorough mixing with high-pressure steam is insured by a jet heater, after which the slurry, now called the "mash," enters a series of U-tubes, at high temperature (360° F.) and under pressure, through which it travels in 60 to 70 seconds. The pressure-cooked mash is flashed to atmospheric pressure and cooled to about 150° F. As the mash leaves the flash chamber, and before it enters the pipelines leading to the fermenters, there is fed into it a malt infusion prepared separately from malted grain, in order to convert the starch from the grain into sugar.

The malt furnishes the enzyme amylase, formerly called diastase, which converts the starch polymer by catalytic hydrolysis into the disaccharide maltose. The saccharification is rapid; it approaches 70 per cent during the travel through the pipeline. The temperature is now lowered further by means of a cooler, and a prepared yeast culture, *Saccharomyces cerevisiae*, is next introduced into the flowing mash stream. The mixture reaches the fermenters at a temperature of 72 or 70° F., which is maintained (cooling) in the fermenters during the reaction. In the fermenters the conversion of starch to maltose goes to completion; the maltase furnished by the yeast hydrolyzes the maltose to glucose, and the zymase attacks the latter, producing alcohol and carbon dioxide, as described in the process using molasses. In some plants, lactic acid-producing bacteria are added to sour the mash in the yeast tub, preventing the growth of foreign bacteria. The fermented mash is the "beer," containing 7 to 8 per cent of alcohol. The beer is pumped to the distilling system. In one large installation, the fermenters are covered steel vessels, circular in cross-section, 20 feet in diameter, and extending through two stories; there are two rows of eight. The fermentation period is two days.

The separation of alcohol from the non-alcoholic substances in the beer is achieved by distillation. The conventional beer still in an industrial alcohol plant is a column with 18 to 20 sieve-type plates topped with 2 to 4 bubble-cap plates; it is operated at atmospheric pressure. Fig. 154 indicates some further details. A different procedure is to run the beer into simple "boilers," whose vapors pass to a continuous purifying and rectifying (concentrating) assembly of columns and stills, as described later. The distillate from the beer column in beverage alcohol plants is collected in glass-lined tanks, inspected, and stored in oak barrels.

After driving out the alcohol from the fermented liquor made from corn, to take a specific example, there is left in the boiler or still a water solution with material also in suspension. The "stillage" is worked up, in the more advanced plants, so that the suspended solids become distillers' dried grain, while the dissolved material becomes distillers' dried solubles. Both are processed as feed products. A yield of 6 to 8 pounds of distillers' dried light grains and 10 to 12 pounds of distillers' dried solubles are obtained from each bushel of grain mashed.

An installation with a continuous cooker system, with a pre-cooker of special design, has been described. A flow sheet for the system shows not

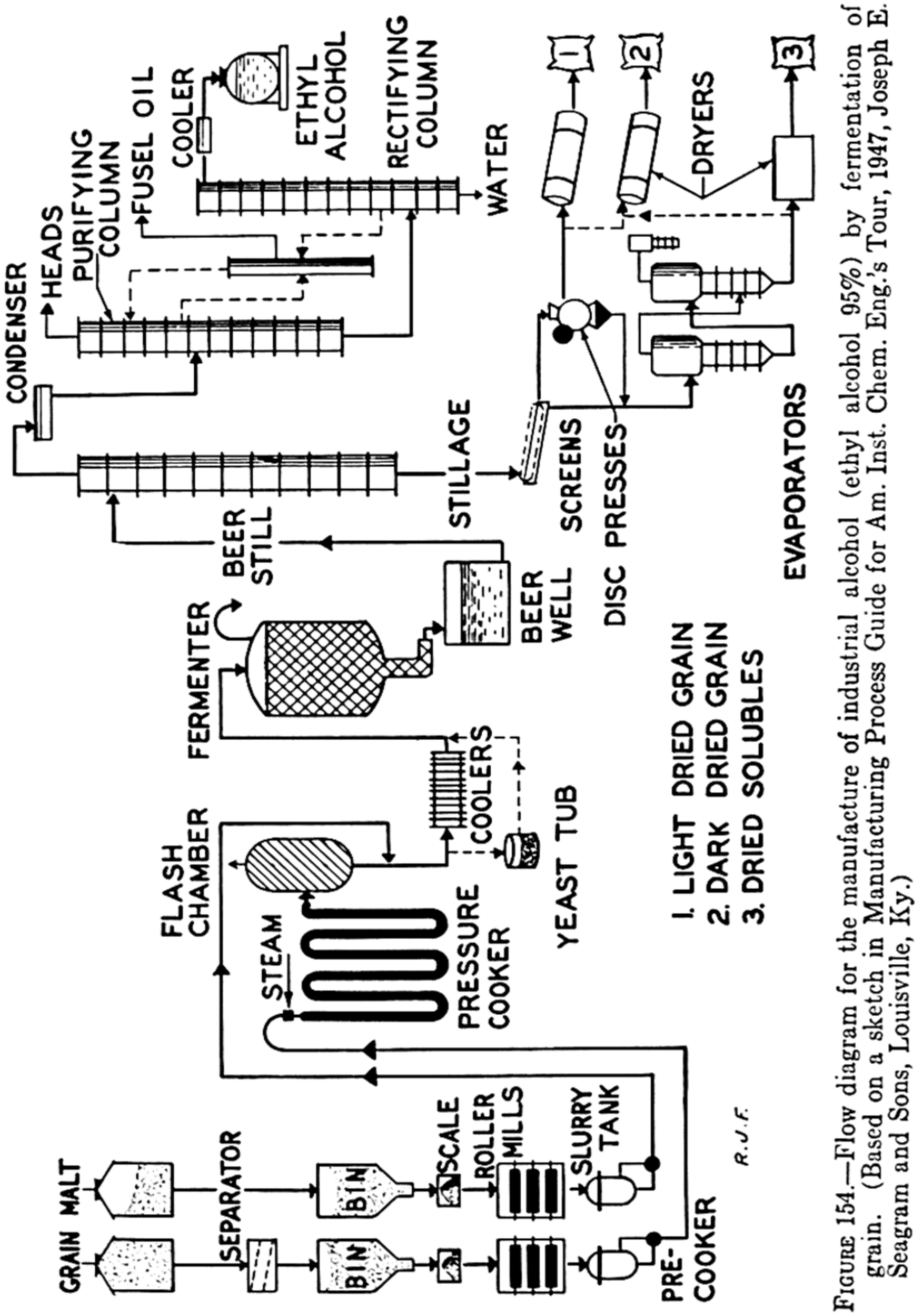


FIGURE 154.—Flow diagram for the manufacture of industrial alcohol (ethyl alcohol 95%) by fermentation of grain. (Based on a sketch in Manufacturing Process Guide for Am. Inst. Chem. Eng.'s Tour, 1947, Joseph E. Seagram and Sons, Louisville, Ky.)

only all equipment, but all the temperatures and the flow in gallons per minute for each vessel and pump.[9]

Potatoes are handled in a similar way and mixed with malt in the proportion of 2 pounds of malt to 100 pounds of potatoes, while for corn, 8 pounds of malt are taken for each 100 pounds of grain. Sweet potatoes may also be used.[10]

Malt can be made in a preliminary operation, or bought from a firm which manufactures it exclusively. Malt is made by the controlled (partial) germination of barley. The barley is first steeped in cold water, then heaped on the floor in the air, and occasionally turned over; the temperature rises, oxygen is absorbed, and carbon dioxide is given off. The germ within the barley (the plumule or acrospire) grows by this process; it contains the desired soluble enzyme, amylase (diastase). Weight is lost; a bushel of barley (48 pounds) produces a bushel of dried malt (34 pounds). The hydrolysis of starch by mineral acids is described later.

A distillery for potable alcohols, such as whiskeys, will operate exactly, up to this point, as described for the industrial alcohol plant, except in the selection of the grade of material. The distillery for potable alcohol takes the product from the beer still, with 45 to 50 per cent alcohol (=90 to 100 proof) and stores it in oak barrels for long periods. The industrial alcohol plant distills the 50 per cent alcohol further to produce 95 per cent alcohol (=190 proof). During the war, all or nearly all the distilleries for potable alcohol became producers of industrial alcohol. There are variations in the equipment and method of distilling 95 per cent alcohol. The operation may be discontinuous, partly continuous, or fully so.

Concentration and Rectification in a Single, Continuous System

One of the earliest and best-known methods for the continuous distillation and rectification of the fermented liquor, with complete separation and purification of the 95 per cent alcohol and by-products, is that of Emile Guillaume.[11] This process has been modified and improved in the intervening years, and others invented, but inasmuch as it illustrates principles common to all, it will be described here.

The Guillaume Process. The essential parts of the Guillaume process are shown in Fig. 155. The apparatus consists of a boiler (not shown), the rectifying column *A*, the purifying still *B*, a vessel *C* to maintain a given alcoholic content, a distilling column *D* for exhausting the charge, the alcohol still *E*, dephlegmators, condensers, and auxiliary apparatus. There is no connection between still *B* and column *D*; a solid metal plate (21) separates them. They are superimposed merely for convenience.

The crude alcoholic vapor from the boiler enters the internal drum, at 2, in the bottom of still *A*, merely passing through on its way to still *B* through pipe 3. This drum is the source of heat in *A*.

[9] "Food for Thought," by Herman Frederick Wilkie and Paul John Kolachov, Indiana Farm Bureau, 1942.

[10] "Dehydrated sweet potatoes for ethanol production," J. A. Jump, A. I. Zarow, and W. H. Stark, *Ind. Eng. Chem.*, 36, 1138 (1944).

[11] U. S. Pat. 887,793, issued May 19, 1908.

All of the boiler vapor arrives in *B*; it is merely somewhat cooler, and partly liquefied. A portion travels down the plates of this column, to meet an entering supply of live steam (entering at 38). The condensate loses aldehydes and all volatile impurities, and reaches the bottom of *B*. The condensate is almost pure. It is conveyed through pipe 4 to the storage vessel *C*.

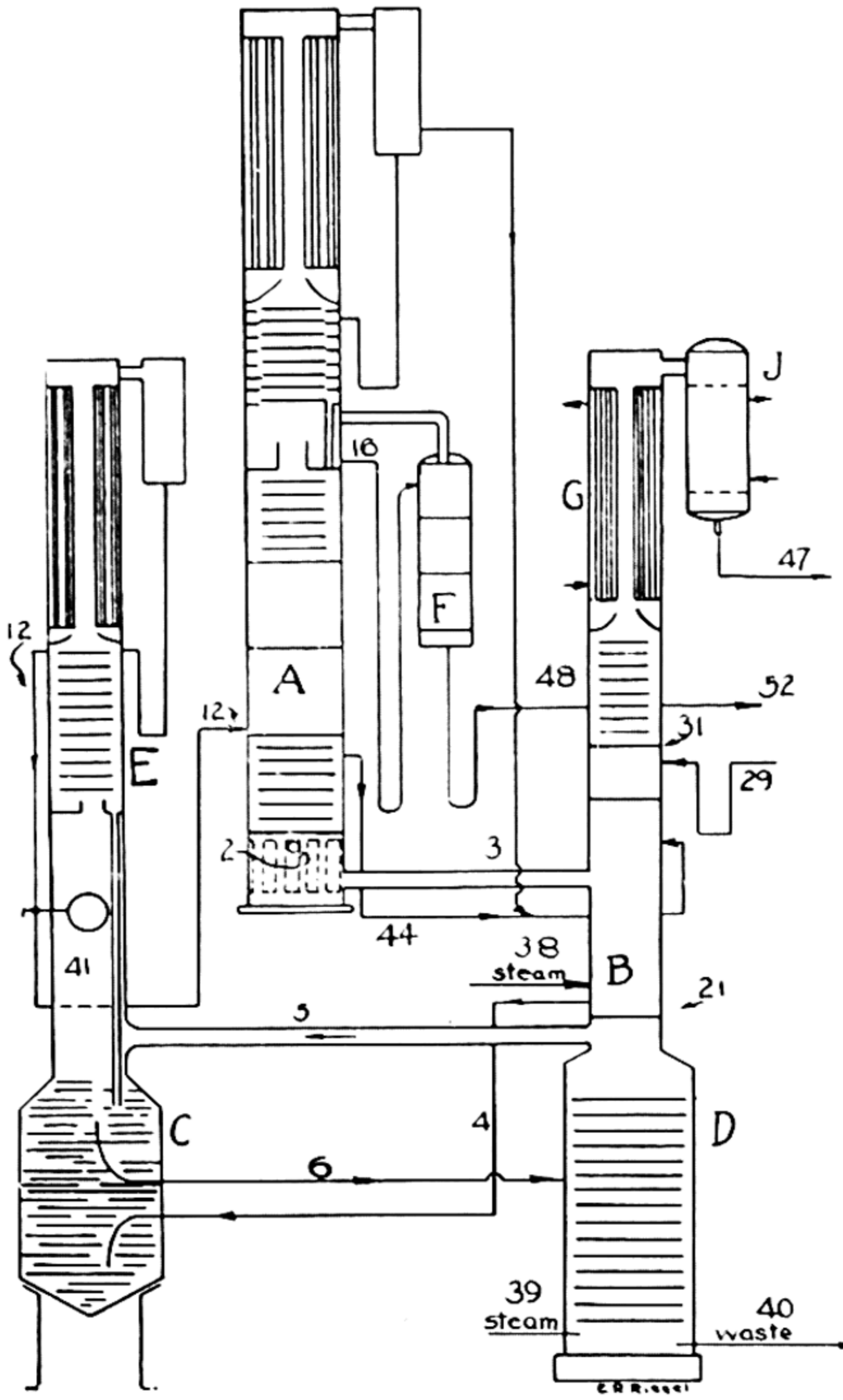


FIGURE 155.—The Guillaume process, for the concentration and rectification by continuous operation of the beer from the fermenting vats. *A*, rectifying still; *B*, purifying still; *D*, weak alcohol still; 41, open still surmounted by alcohol column. *C*, storage vessel for hot hydrous alcohol. *F*, short column still for final purification. The pure product leaves the system by line 52. (See text for other parts.)

In *B*, the volatile impurities travel upward, being at the same time fractionated. A regulated stream of water is added at 29, in order to dilute the alcohol sufficiently (30 to 33 per cent by weight) to hold it back. The fusel oil is drawn off at 31, to be fractionated further in a separate apparatus; this fraction contains amyl alcohol, amyl valerate, ethyl acetate, ethyl isovalerate, ethyl butyrate, and similar bodies. Escaping condensation in the dephlegmator *G*, the aldehydes and formate esters pass into condenser *J* and from there, now liquid, to receiving vessels.

By adding water at 29, the various esters and higher alcohols can be distilled away from the alcohol without any great amount of alcohol distilling. This is because the esters and higher alcohols are comparatively insoluble in water and do not suffer a reduction of vapor tension due to water admixture as does ethyl alcohol.

The purified, weak alcohol in *C* is delivered at a continuous rate to the still *D*, where it travels downward over the plates, meeting live steam which enters the column *D* at 39. There passes out of *D* to the open column 41 a vapor containing all the alcohol and considerable water; it reaches column *E* where it is condensed, fractionated and concentrated in the usual way. The product from *E* is 86 per cent alcohol, still purer than when it entered vessel *C*, for a small amount of amyl alcohol is removed from the

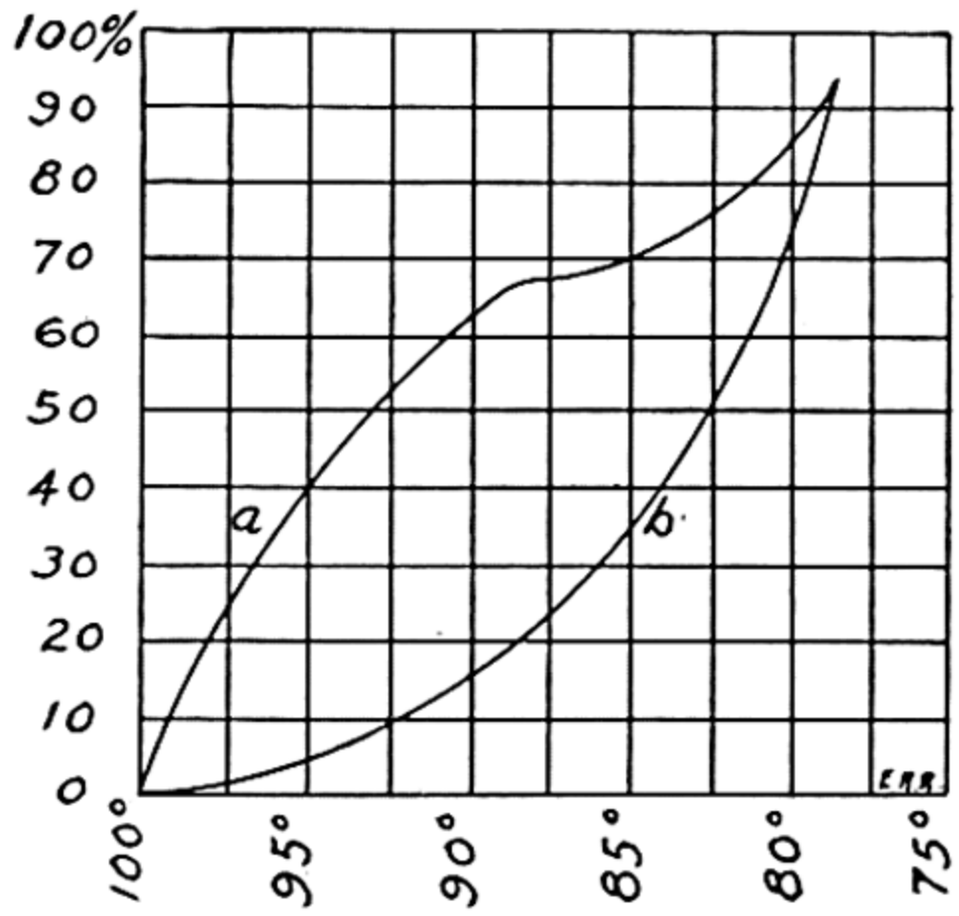


FIGURE 155a.—Difference in composition between the vapor and the liquid for alcohol-water mixtures. Abscissas, boiling temperatures; ordinates, percentages of alcohol in *a*, the vapor; *b*, the liquid. Example: At 90° C., the liquor has 16% alcohol, but the vapor rising from it has 62%.

lower plates and sent to 48; it leaves *E* at the upper plate through line 12 leading to the bottom of still *A*, where the final rectification to the full strength takes place. A weak residue passes out of *A* through pipe 44 and is returned to the system at still *B*. The strong alcohol leaves *A* through pipe 16. It is passed through a supplementary column, *F*, for a final purification of such esters as were formed during the process of distillation, by oxidation and esterification. The treated, now very pure alcohol of 95 to 96 per cent by weight, leaves the bottom of *F* by line 52.

The flow of the various liquids is regulated by valves and a control mechanism located in open still 41, and depends upon the temperature of the vapors.

In one of the continuous processes for the production of 95 per cent alcohol, the addition of water is avoided; only water-vapor in the form of steam is injected.[12] Ethyl alcohol from wood cellulose has been described in Chapter 16.

The concentration of aqueous alcohol is possible because when it is vaporized, the vapor is richer in alcohol than the liquid from which it rises (*see* Fig. 155a). There is at each plate of the still an enrichment of the vapor, which rises to the next plate, there to gain in alcohol again, while the liquid descends, to meet on the lower plate a leaner vapor to which it

[12] U. S. Patent 1,835,848.

loses alcohol. The paths of vapor and liquid are countercurrent. Pure alcohol (ethyl alcohol, C_2H_5OH) boils at 78.5° C., water at 100° C.; starting with an aqueous alcohol, the gain in alcohol in the vapor continues until 97.2 per cent by volume is reached; beyond that the vapor no longer differs from the liquid from which it rises (constant-boiling mixture, with boiling point 78.174° C.); for this reason, 97.2 per cent alcohol is the highest strength obtainable by distillation alone. Industrial alcohol contains 95 per cent alcohol; the remainder is water.

"100 U. S. proof" is composed of 50 per cent of alcohol and 50 per cent of water by volume. "200 proof" is pure alcohol. The "100 British proof" is slightly stronger than the 100 U. S. proof. Alcohol of 100 U. S. proof will burn when touched with a match.

Synthetic Industrial Alcohol. For the manufacture of ethyl alcohol from ethylene, the gas (32 to 100 per cent C_2H_4) enters near the bottom of an absorber (a plate tower, for example,[13] of acid-resisting metal), where it meets a descending stream of concentrated sulfuric acid.

$$2C_2H_4 + H_2SO_4 \rightarrow (C_2H_5)_2SO_4$$

The pressure is 200 to 500 lbs per sq in. and the temperature 180° F. (82° C.). Heat is evolved during the absorption, so that cooling coils must be provided to keep the temperature at the desired point. The unabsorbed gases are scrubbed with water and released to the atmosphere. The liquid product issuing from the base of the tower contains ethyl sulfate, ethyl hydrogen sulfate and sulfuric acid; it is cooled, and then mixed with water; the mixture is then pumped to a hydrolyzer, where alcohol is formed and a dilute sulfuric acid regenerated.

$$(C_2H_5)_2SO_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2SO_4$$

The mixture enters near the top of a stripper column; alcohol vapors pass out overhead, while the residual liquid is thoroughly exhausted by means of a reboiler. The alcohol vapors are scrubbed with water (or caustic) and collected as raw alcohol. The latter is freed of the ether it contains (about 5 per cent) in the ether column by means of steam, and is concentrated in the rectifier, giving 95 per cent alcohol as overhead product. Bottoms from the rectifier are run to waste. The dilute sulfuric acid (50 per cent) is concentrated to 95 per cent H_2SO_4 (see Chapter 1) and is reused.

A process for the direct hydration of ethylene to alcohol is just entering the commercial stage.[13] A water-ethylene mixture, at 200° C. (392° F.) in the ratio of 2 to 1, under a pressure of 300 lbs per sq in., passes through an alumina catalyst, when a 20 per cent conversion is obtained:

$$C_2H_4 + H_2O \leftrightarrows C_2H_5OH$$

The alcohol formed is removed by cooling and the gas, mixed with make-up gas, is recycled. The synthetic alcohol is equal in quality to the best grade made by the fermentation process.[13]

[13] "Synthetic alcohol from petroleum," Robert S. Aries, *Petroleum Refiner*, 27, 203 (1948); "Production of synthetic alcohol from ethylene," C. M. Beamer, *Chem. Eng. Progress*, 43, 92 (1948), with a flow sheet and many charts of prices and uses.

Ethyl alcohol will be separated from other products present in the oxygenated portion of the products in the synthetic liquid fuel process (Chapter 24).

Cost, Production and Uses of Industrial Alcohol. The cost of industrial alcohol will depend upon the cost of the raw material, the cost of fuel,[14] and the efficiency of the fermentation or process. Two and a half gallons of molasses make one gallon of industrial alcohol (95 per cent); the price and the supply of molasses have fluctuated, but taking a figure of 15 cents a gallon (which is below recent quotations), the raw material alone would be 37½ cents. The cost of conversion is upward of 4 cents, and the overhead, materials and labor for denaturing is at least another 4 cents a gallon. The quotation (December 6, 1948) for ethyl alcohol (95 per cent), tax-free, in drums, carload lots, was 58.5 cents a gallon; in car tanks, 49 cents. The denatured grades were listed at 61½ cents, in carload lots. It has been estimated that industrial alcohol from corn would cost, with corn at 45 cents a bushel, 30 to 32 cents a gallon; one ton of corn (33 bushels) yields close to 90 gallons of 95 per cent alcohol. Industrial alcohol made from sulfite waste, 20 to 30 cents; from ethylene under the most favorable conditions, 15 cents; while that made in the synthetic liquid fuel process may cost 7 to 8 cents a gallon.

Table 64 shows the great variation in the relative amounts of the several raw materials used in two different years, and their respective percentage of the total alcohol produced.

TABLE 64.—*Materials used at industrial alcohol plants in the production of undenatured ethyl alcohol, fiscal year ending as shown.**
(Selected items.)

	Quantity used	June 30, 1947 Ethyl alcohol produced in proof gallons (=50% by vol.)	% of total
Ethyl sulfate	106,456,844 gallons	133,305,506 proof gallons	44.60
Molasses	70,305,871 gallons	54,158,717 " "	18.12
Products used in redistillation	50,082,760 proof gal.	49,546,332 " "	16.58
Grain	509,569,387 pounds	39,742,438 " "	13.30
Potatoes	526,455,909 pounds	12,861,322 " "	4.30
Sulphite liquor	205,336,430 gallons	4,379,771 " "	1.32
Cellulose pulp and alcohol mixtures	3,700,122 gallons	2,422,135 " "	0.81
Total made		298,881,399 " "	100
		June 30, 1948	
Molasses	174,363,824 gallons	142,328,423 proof gallons	38.75†
Ethyl sulfate	109,244,594 gallons	140,228,078 " "	38.18
Grain	421,464,538 pounds	34,657,791 " "	9.44
Products used in redistillation	34,977,137 proof gal.	34,515,122 " "	9.40
Sulphite liquor	237,364,270 gallons	5,187,590 " "	1.41
Cellulose pulp and alcohol mixtures	2,983,599 gallons	1,943,912 " "	0.53
Total made		367,259,285 " "	100

* U. S. Treasury Dept., Bureau of Internal Revenue, Alcohol Tax Unit.
† In 1941, molasses accounted for 70.41 per cent of total production.

[14] The fuel required is estimated at 11 pounds of coal per gallon.

The greater part of the industrial alcohol in trade channels continues tax-free, mainly in the form of denatured alcohol. In the year ending June 30, 1947, withdrawals for denaturing were 338,029,989 proof gallons, in the next year 301,101,168 proof gallons. In the United States, there are two classes of denatured alcohol: completely denatured, which may be sold without a permit, and specially denatured alcohol. The standard denatured alcohol for radiators contains, to 100 parts 80 per cent ethyl alcohol, 5 of isopropanol, 0.75 of aldehol A, 0.75 of alcotate, 0.25 of terpineol (1933). Aldehol is the name given a liquid made by blowing air through boiling kerosine. There are over 30 specially denatured alcohol formulas suitable for specific purposes. These are sold to manufacturers who may select denaturing materials which have no effect upon their particular processes.

Over the period of World War II, the demand for industrial alcohol was at an exceedingly high rate, as shown in Table 65, which covers 2½ years.

TABLE 65.—*War-time consumption of ethyl alcohol (industrial alcohol) 190 proof, equivalent to 95 per cent*

(January 1, 1943, to June 30, 1945)*

	Gallons
Direct military	82,200,000
Lend-lease	142,900,000
Synthetic rubber	611,200,000
Antifreeze	92,100,000
Indirect military and civilian	389,100,000
Total consumption	1,317,500,000

* "Facts for Industry," Bureau of the Census.

Denatured alcohol is used as a solvent for shellac (2.5 million gallons), in plastics (3.8), in proprietary solvents (21), in face lotions and other toilet preparations (6.08), for processing nitrocellulose and food and drug products (12), in pharmaceutical preparations (1.3); and as a raw material in the production of chemicals (102.8).

Alcohol serves also as a fuel in lamps and burners, both in the form of a liquid and of "solidified alcohol," [15] and in internal combustion motors; the latter is susceptible of considerable development which depends upon the supply of crude oil and gasoline, and on the price of alcohol.

BREWING INDUSTRY

Beer is made by boiling in the presence of hops certain extractable materials contained in malted barley and other grains, and then fermenting this brew by the addition of brewers' yeast. The methods employed by breweries in the preparation of beers and ales differ in important details in the various establishments, yet they are sufficiently similar to be represented by

[15] U. S. Pat. 1,262,282, Jacob Schaub. A solution of nitro-cellulose in denatured alcohol containing a little acetone, pyridine and cracked kerosene is placed in the can and a small amount of water in a fine stream is squirted into it; the entire content of the can changes to a gel which does not liquefy when heated. Earlier processes employed soap or calcium acetate in water solution; in 1,208,265 (to C. Baskerville) the proportions and ingredients are 10 to 15 per cent saturated calcium acetate solution, 85 to 90 per cent industrial alcohol, 0.5 to 1.0 per cent stearic acid.

those practiced in a typical brewery in upper New York State, which will be described.

The capacity of the plant is 600,000 barrels per year (1 barrel-31 gallons). The raw materials are rice, corn grits, both of them oil-free, wheat flakes, sometimes soybean, malt, hops,[16] and some others in smaller quantities. Besides these, pure yeast and an abundance of water are required for making the beverage itself and for cooling. The corn grits, which must be free from germ, and the rice, for example, are taken in quantities sufficient to furnish 30 to 40 per cent of the required starch, while enough malt is added to furnish the balance. After passing cleaners and crushing rolls, the rice and the corn, made up with water, and with the addition of some malt, are heated in a pressure cooker with an agitator under 5 pounds pressure for 45 to 60 minutes. The action is mainly the liquefaction of the starch. The main portion of the malt, made up with water, is placed in the mash tub, which is just like the cooker, and thoroughly mixed at a temperature between 100 and 120° F. and then allowed to rest. During the rest period the proteolytic enzymes begin to degrade the malt and other proteins into soluble forms. After this period the contents of the cooker are added; these raise the temperature to 149 to 158° F., at which point the material is held for conversion. The temperature is then raised to 167° F., which is high enough to arrest the action of the conversion. The purpose of mashing is first to extract from the malt its starch and ferments, including the diastase, which changes the starch to sugars during the conversion period. The material next passes to the Lauter tub whose bottom has slots through

TABLE 66.—*Analyses of brewery products, January, 1949.*

	Indian Head Lager	Indian Head Ale
Appearance on arrival	clear	clear
Color	5.75° Lovibond	6.0° Lovibond
Odor	Pure	Mildly aromatic
Taste	Pure, somewhat full-bodied, good hop flavor	Pure, vinous, good hop flavor
Foam-keeping capacity	Good	Good
Specific gravity	1.01598	1.01399
Saccharometer indication	4.07° Plato	3.57° Plato
Alcohol, by weight	3.80%	4.20%
Alcohol, by volume	4.89%	5.40%
Extract	5.79%	5.49%
Sugar	1.63%	1.54%
Dextrin	2.52%	2.23%
Unconverted starch	None	None
Acidity as lactic	0.16%	0.16%
Protein	0.40%	0.42%
Heavy metals	None	None
p_H value	4.60	4.30
Carbon dioxide, 2 bottles	0.48%, 0.48%	0.45%, 0.45%
Original gravity	13.1° Plato	13.6° Plato
Real degree of fermentation	55.8%	59.6%
Apparent degree of fermentation	68.9%	73.8%
Chilling test, clarity (absolute turbidity) on 2 bottles chilled 24 hours in ice pack	a.—0.0029. b.—0.0030	a.—0.0028. b.—0.0028

[16] The hops are kept in a refrigerated room; otherwise they develop a resinous odor, and are valueless for making beer.

which the clear liquor, or wort, passes while the arms of the agitator turn slowly. "Sparge water" in spray form is introduced to exhaust the material on the screen. The wort is run into the boiling kettle, a jacketed copper kettle with capacity, in this plant, of 450 barrels. During the period of boiling, which lasts 2½ to 3 hours, the hops are added at fixed intervals. While in the kettle, the enzymes are destroyed, the hop "bitter" is extracted, undesirable proteins are coagulated, other proteins are precipitated by the tannin in the hops, and the whole is sterilized by the heat. There is also a concentration of about 10 per cent. The material next is strained to remove all solids, especially the spent hops, and the clear liquor, after settling for a while in the hot wort tank, is run over coolers such as the Baudelot, and from there to fermenters which may be of wood, glass-lined steel, or aluminum. Here the yeast is added, for example, ¾ pound liquid yeast per barrel. The fermentation lasts seven to ten days, after which the beer is run through a cooler into glass-lined storage tanks which in this plant have a capacity of 60,000 barrels. Here some 5 to 15 per cent of beer in high state of fermentation is added to the fully fermented beer and is allowed to work out; as it ferments it provides the carbonation, for the tank is sealed to a pressure of 6 to 8 pounds. The beer absorbs the carbon dioxide. After a period of a week or more the beer is filtered through a mass filter under pressure; it is recarbonated sufficiently while passing through the pump, at a temperature of 32° F., to bring the carbon dioxide content to 0.48 per cent in the final beer, and the product is bottled or barreled. The carbonation may be performed entirely by pumping sterile carbon dioxide into the cooled beer from the fermenters. The bottled beer is pasteurized at 140° F. (60° C.) after capping.

Absolute Alcohol on a Commercial Scale

In addition to industrial alcohol, there is on the market, in drum and carload lots, 100 per cent ethyl alcohol, called absolute alcohol, which has properties of miscibility not possessed by industrial alcohol. Absolute alcohol is miscible with gasoline in all proportions, while industrial alcohol is not. In order to make a motor fuel from gasoline and alcohol, a fuel which must be a single liquid, a third component must be added, such as benzene, ether, or tetralin.

Such blended motor fuels are important in countries which must import their petroleum products. There have been proposals in the United States to add 5 per cent alcohol to gasoline, as a "farm relief" measure; to date, they have come to naught.

Absolute alcohol is used largely as an automobile antifreeze, after denaturization, for which purpose, ironically enough, it is diluted with water. An important demand for absolute alcohol comes from the lacquer industry, in which it is a valuable solvent. Thanks to several continuous methods, absolute alcohol is obtainable at reasonable prices.

The Keyes Process. In the process patented by Donald B. Keyes,[17] advantage is taken of the fact that on addition of a third constituent such

[17] U. S. Patent 1,830,469.

as benzene (= benzol) to the alcohol and water present in 95 per cent alcohol, a three-constituent mixture, or ternary mixture, with a constant, low boiling point, is formed, and this mixture may be driven out, leaving the greater part of the alcohol free from water in the lower part of the still. The benzene as well as the alcohol in the ternary mixture may be recovered completely by suitable secondary operations. This is facilitated by the interesting fact that on cooling, the ternary mixture condenses to form two

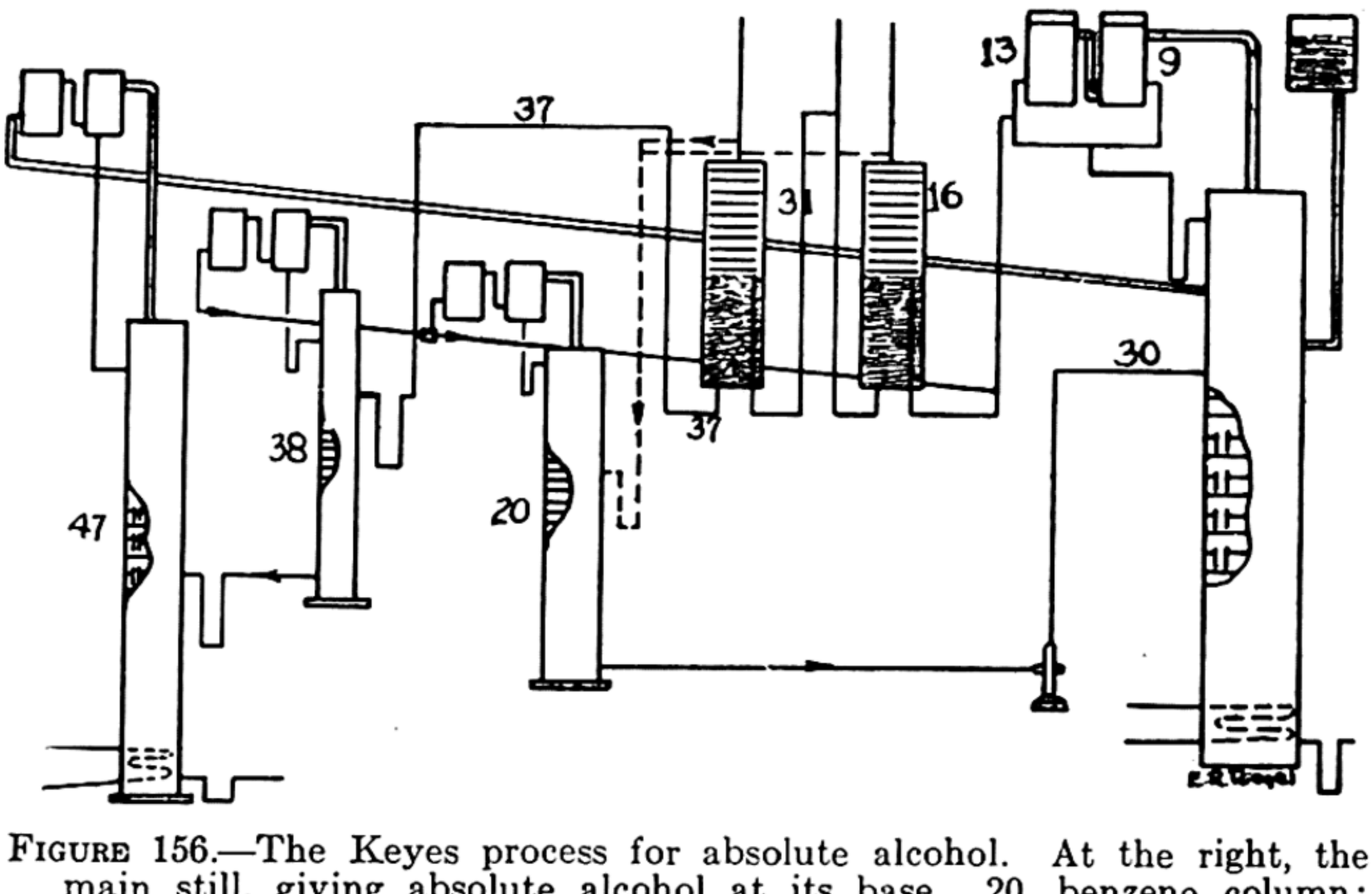


FIGURE 156.—The Keyes process for absolute alcohol. At the right, the main still, giving absolute alcohol at its base. 20, benzene column; 38, alcohol rectifying column; 47, alcohol recovery column. (For other parts, *see* text.)

immiscible layers, the upper containing most of the benzene, the lower, most of the alcohol. By means of a separator, these two layers are divided, and sent to different rectifying stills.

The ternary constant boiling mixture boils at 65° C., and contains

Alcohol	18.5% by weight
Benzene	74.1%
Water	7.4%

It boils considerably lower than pure, dehydrated alcohol (78.5° C.).

On condensing, this ternary mixture forms two separate, immiscible layers, which have, at 28° C., the following composition:

	Upper layer	Lower layer
Alcohol	11.6% by weight	51.3% by weight
Benzene	85.6%	8.1%
Water	2.8%	40.6%

Of the total, the upper layer is 84.7 per cent, the lower, 15.3 per cent, all by weight.

The procedure will be described in greater detail, with the aid of Fig. 156. Industrial alcohol is fed into a 40-plate still, the main still, at the tenth plate from the top. Benzene is introduced, in an amount sufficient

to form the constant-boiling mixture with all the water present. Fractionation takes place, the liquid becoming richer in alcohol as it descends, while the vapors of the ternary mixture pass out at the top of the still. These vapors reach dephlegmator 9, which is kept at 65° C., so that any excess alcohol vapor is condensed and runs back to the still; they continue to condenser 13, where they liquefy, and from there run into separator 16, where the two layers form. Heat is supplied to the still by a steam coil; the temperature at the base of the still is 79° C. The absolute alcohol is drawn off at that point, cooled and stored.

The upper or benzene layer in 16 passes to the benzene column, 20, heated by a steam coil (indirect heat). There rises the ternary constant-boiling mixture, consuming all the alcohol and water, but leaving the excess benzene. This latter is drawn off, cooled, and pumped back into the main still through pipe 30.

The lower layer in 16, which might be called the water layer, passes to scrubber 31. Water is run in, and two layers form again; the upper layer is run to column 20, where its benzene is abstracted. The lower water layer goes through pipe 37 to column 38, heated again by a closed steam coil. The ternary mixture rises, this time exhausting the benzene, leaving the excess alcohol and water in the still. The vapors are dephlegmated and then condensed, and pass to 16. From the bottom of 38, a 30 per cent alcohol is drawn and sent to the alcohol recovery column 47, which sends out at its top in vapor form 95 per cent alcohol, and allows removal at its base of the water. The heat for this column is also indirect. This process has been in successful operation for some years.[18]

Other substances instead of benzene may be used as the third constituent in the ternary mixture which is essential to this process; for example, ethyl acetate, carbon tetrachloride, or hexane.

Another process which uses a water-immiscible liquid as a means of removing the water from 95 per cent alcohol to produce absolute alcohol is the Steffens process.[19]

The Glycerin Process. In the process patented by Joseph Van Ruymbeke[20] a different principle is applied. A countercurrent of glycerin is allowed to flow through the still, downward, while the alcohol-water vapor rises. The glycerin acts as dehydrating agent, finally reaching the bottom of the still with all the water combined with it, while the alcohol vapors passing out of the top of the still are low in water, or free from water, depending on the volume of glycerin relative to the volume of 95 per cent alcohol used. The more the relative amount of glycerin, the drier the alcohol. In order to produce 1000 liters of 98 to 99 per cent alcohol, 1000 liters of glycerin must be fed in at the top of the still.

The glycerin and water passing out at the bottom of the still contain also a considerable amount of alcohol. The alcohol is recovered in a second rectifying still, in which the glycerin-alcohol-water solution passes down,

[18] Although absolute alcohol made by this process is essentially pure, it retains enough benzene to give the absorption bands of benzene, in the ultraviolet region.

[19] U. S. Patent 1,670,053.

[20] U. S. Patent 1,459,699.

while steam, injected at the base of the still, passes upward. The alcohol-water vapors passing out at the top of the still are concentrated in other stills in the usual way, while a water solution of glycerin is obtained at the bottom. This dilute glycerin is concentrated as explained in Chapter 32, and may then be used over again.

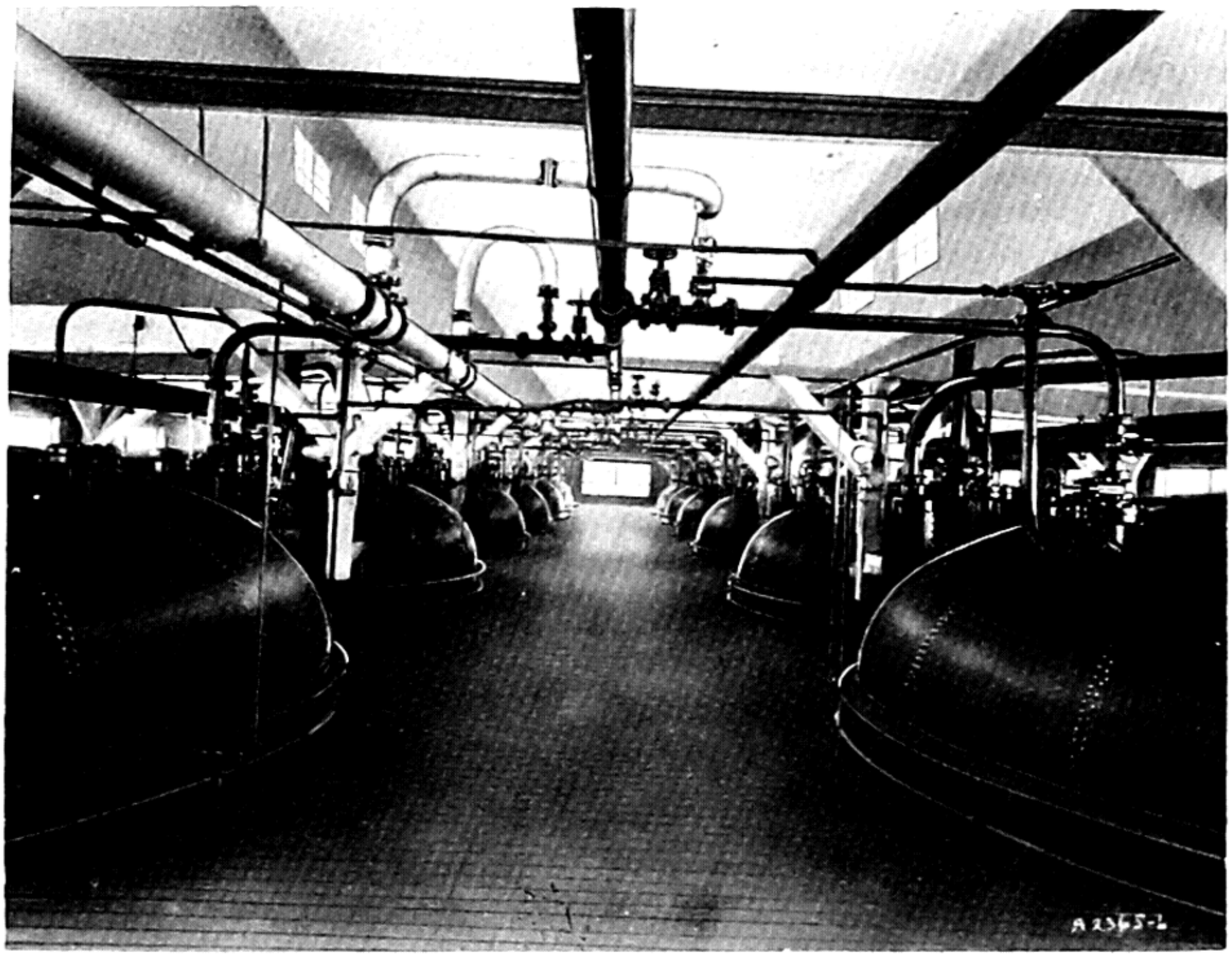


FIGURE 157.—Butyl alcohol fermentation tanks of 50,000 gallon capacity each; only the top of tank is shown at upper level; the tanks extend through the floor to lower level. (Courtesy of the Commercial Solvents Corporation, Terre Haute, Ind.)

In a later patent,[21] the same inventor adds dehydrating salts, such as $ZnCl_2$, $CaCl_2$, K_2CO_3, to the glycerin, and obtains alcohol with 99.8 per cent content.

ACETONE AND BUTYL ALCOHOL

Acetone and butyl alcohol are obtained by the bacterial action of selected organisms on corn or other carbohydrate. (*See* Figs. 157, 158.) In the Fernbach-Strange process,[22] the organism is designated as "of the type of the butylic bacillus of Fitz," and is allowed to act at 30° to 35° C. in the absence of air; 50 per cent of the malted starch is changed, to give acetone and butyl alcohol in the proportions of 1 part acetone to 2 parts of butyl alcohol. In the Delbrueck-Meisenberg process,[23] the *Bacillus macerans* is spread on fruit peel, asbestos, or other inert material with large surface; the solution containing the sugar with the necessary nutritive material, the same

[21] U. S. Patent 1,474,216.
[22] U. S. Patent 1,044,368 (1912).
[23] U. S. Patent 1,169,321 (1916).

as for yeast, is added; after 5 days the action is complete; 90 per cent of the sugar (best as molasses) is changed to acetone and butyl alcohol. In the Weizmann process,[24] corn is very suitable; the organism is *Bacillus clostridium acetobutylicum*, cultivated from organisms originally found on the surface of the corn and other cereals.

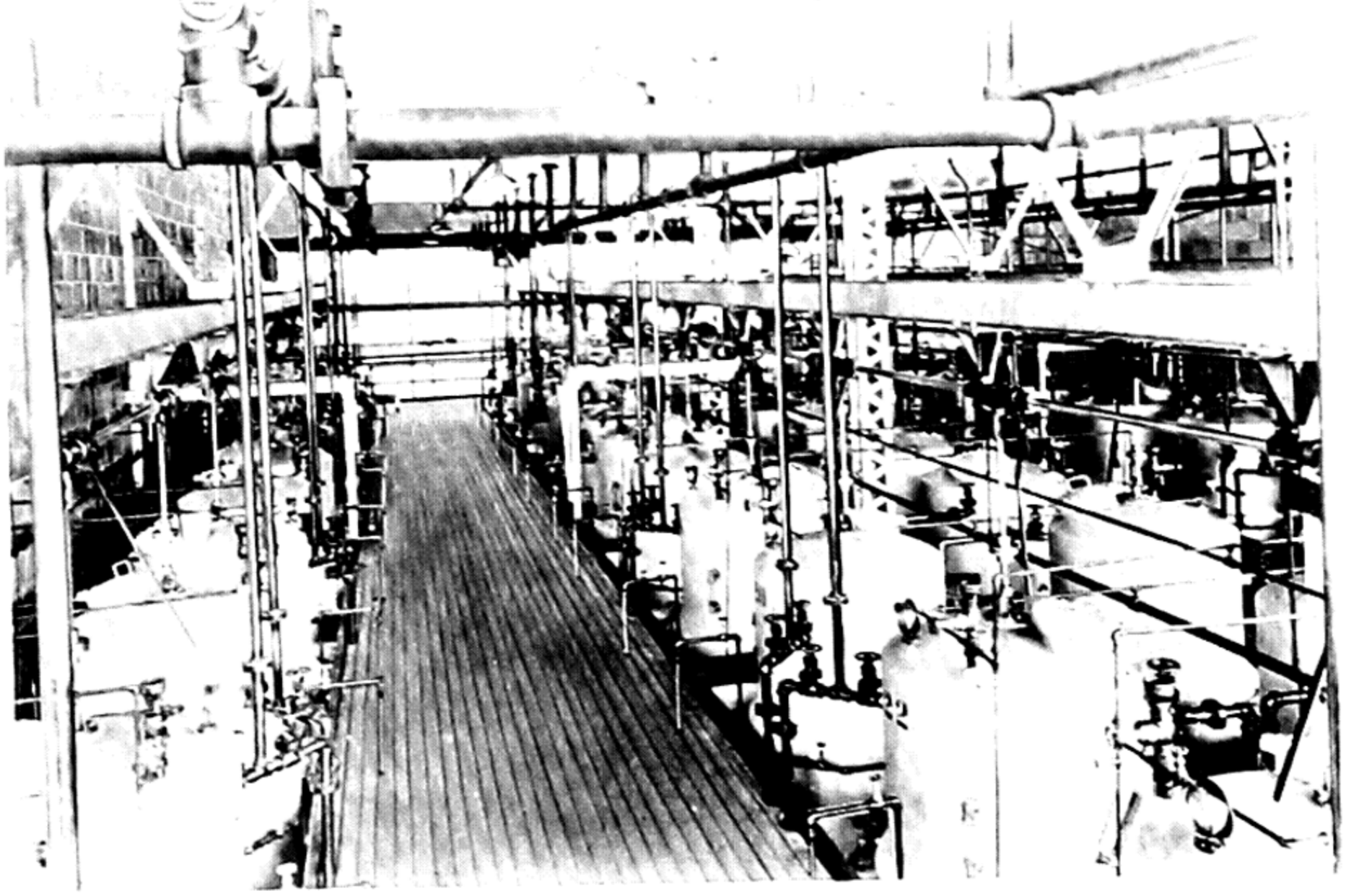


FIGURE 158.—800-gallon bacteria-propagation tanks for butyl alcohol fermentation; one tank furnishes the right amount of culture for one 50,000-gallon fermentation tank. (Courtesy of the Commercial Solvents Corporation, Terre Haute, Ind.)

The process is as follows: The crude starch from the corn (Chapter 23) is mixed with water in the "mash tuns," then run to the "cookers," closed vessels in which the suspension is heated, giving a thick, sterilized starch paste. After cooling to 98° F. in water-jacketed coils, the starch paste enters the fermenting tanks; a charge of bacteria culture is added, 800 gallons of culture to 40,000 gallons of paste. The action begins after four hours; the jelly-like starch paste begins to liquefy, gradually becoming a thin, watery liquid. At the same time, gases are evolved and pass out with great violence. Gradually the foaming subsides, and 48 hours after the addition of bacteria to the paste, the action is over. The starch has been converted into liquid products and gases (hydrogen and carbon dioxide). The liquid products are formed in the ratio of 6 parts butyl alcohol, C_4H_9OH, 3 parts acetone, and 1 part ethyl alcohol.

Extreme care is used to protect the *Clostridium acetobutylicum* from outside influences which might decrease its activity. A supply of the pure

[24] Brit. Patent 4,845 (1915).

organism is always at hand, and more put away, mixed with dry, sterilized earth, in which condition it lies dormant for months and even years. A little of the earth is placed with an ounce of starch paste in a test-tube, kept at 98° F.; after one day, it is liquid, and the ounce is placed in a quart of the paste. In one day, this is liquid, and is placed in a 10-quart flask; at one day's interval, transfer is made successively to an 80-quart lot in an enamel tank, then to the final 800-quart batch. Each fermenting vat receives a culture made directly from the dry earth bacteria, over a period of five days.[25]

The purification consists of the following steps: The product of bacterial action, called the "beer," is distilled in order to separate all the volatile substances from the non-fermented residue. The distillate is next separated by a second distillation into the acetone fraction (boiling point 56° C., 132.8° F.), the ethyl alcohol fraction and the butyl alcohol fraction. All three are refined further; the refining of the last is done in accordance with an interesting patent.[26]

The hydrous butyl alcohol is distilled in a column still with plates, heated by a steam coil; as received from the previous distillation, it contains water. There passes over a constant-boiling mixture containing 70 per cent butyl alcohol and 30 per cent water, at 90° C. (194° F.); on cooling, this distillate separates into 2 layers, an upper layer with 20 per cent water and 80 per cent butyl alcohol, and a lower layer with 96 per cent water and 4 per cent butyl alcohol. The lower layer is drawn off and sent through the beer stills again; the upper layer is returned to the still, where it forms once more the 30 per cent (water) constant-boiling mixture, which passes out. The vapors passing out carry more water than the liquid returned, so that the still gains in butyl alcohol, and loses in water. Some excess alcohol vapor passes out with the constant-boiling mixture, but is returned to the still by a dephlegmator kept at 95° C. (203° F.), which condenses it (boiling point 117° C., 242.6° F.), while it allows the 70 per cent mixture to pass out to the cold condenser. Finally the still contains only anhydrous butyl alcohol; this condenses on the upper three plates, free from any impurity, and may be drawn off from there.

Butyl alcohol itself is a solvent in lacquers; besides, it serves to make butyl acetate, a still more valuable and important solvent (*see* table of manufactures), and a number of other esters. Butyl alcohol is manufactured not only by fermentation, but also by synthetic processes. In 1946 230,537,000 pounds of butyl alcohols (100 per cent) by all processes were produced (13 cents a pound). In the same year, the production of acetone by fermentation was 37,436,000 pounds, and from isopropyl alcohol $CH_3CH(OH)CH_3$ by catalytic dehydrogenation, 298,148,000 pounds (6 cents a pound).

The hydrogen and carbon dioxide gases from the fermentation tanks are utilized in the catalytic synthesis of methanol, one of the most brilliant achievements in chemical technology (Chapter 25).

[25] From a description kindly furnished by the Commercial Solvents Corp., Terre Haute, Ind.

[26] U. S. Patent 1,394,232 (1921).

During World War I both acetone and ethyl alcohol were greatly needed, while the demand for butyl alcohol was limited. Efforts were made to develop an organism which would produce acetone and ethyl alcohol only; one such investigation resulted in the culture of a new organism, which was called *Bacillus acetoethylicum*.[27]

Synthetic amyl alcohol, to which reference has already been made in this chapter, is obtained by chlorinating pentane, a low-boiling fraction (28° to 37° C. or 84° to 96° F.) of casing-head gasoline.[28] The chloropentane is then hydrolyzed, giving normal amyl alcohol; amyl alcohol from fusel oil is a mixture of iso-amyl alcohol and optically active (dextro) amyl alcohol.

Lactic Acid. Lactic acid is formed by the action of *Bacterium lactis acidi* on molasses or other sugar-containing material. After dilution, chalk is added, and a nutritive solution, and the action allowed to take place at 40° to 45° C. (104° to 113° F.); the chalk is acted on by the lactic acid as fast as formed, and carbon dioxide given off:

$$2CH_3CHOHCOOH + CaCO_3 \rightarrow (CH_3CHOHCOO)_2Ca + CO_2 + H_2O.$$

The chalk must be added because the bacteria become inactive if the concentration of the acid is allowed to rise above 1 per cent. The calcium lactate precipitates and is filtered, washed, and treated with dilute sulfuric acid which liberates the lactic acid in solution form. The calcium sulfate is filtered off, the solution of lactic acid clarified, and concentrated to 50 per cent lactic acid, a thick solution. Pure racemic lactic acid melts at 18° C. The 50 per cent solution is used in textile plants, and, especially purified, in certain foods.

The souring of milk is due to the same organism, which forms lactic acid from the sugar in the milk, the lactose.

The production of lactic acid in 1946 was 6,043,000 pounds, of which 3,824,000 pounds were of the edible grade.

Citric Acid. Citric acid by fermentation is made by the action of the mold *Aspergillus niger* on sugar (sucrose, *l*-fructose, or *d*-glucose). A 14 to 20 per cent sugar solution containing nutrient salts is spread in shallow, open aluminum pans, inoculated with a culture of *A. niger* and held at 28° C. (82° F.). The pH is adjusted at 2.2 at the start. The low pH is favored because it suppresses the formation of oxalic acid. The mold grows until finally there is formed a matt over the whole surface, in a period of 7 to 12 days, when the fermentation is complete. The mycelium is removed and the liquid treated with milk of lime. The calcium citrate formed is separated, suspended in sulfuric acid, and the solution of the liberated citric acid filtered free of calcium sulfate, purified, concentrated in lead-lined steel evaporators and then crystallized, with agitation,[29] to form granular citric acid monohydrate, or at rest, to give large transparent crystals, both having the formula $COOH \cdot CH_2 \cdot C(OH)(COOH) \cdot CH_2 \cdot COOH \cdot H_2O$. The

[27] *Ind. Eng. Chem.*, 11, 723 (1919); or U. S. Patent 1,293,172.

[28] "High-boiling solvents from natural gas pentanes," Lee H. Clark, *Ind. Eng. Chem.*, 22, 439 (1930).

[29] U. S. Pat. 1.921.634.

anhydrous form (opaque anhydrous citric acid) may be made directly from a hot solution by crystallizing at 40° to 100° C. under a high vacuum (730 mm).[30] The opaque anhydrous form formerly in demand for tableting, was made by heating the monohydrate in air under controlled temperature conditions.[31]

Citric acid of commerce is produced additionally from lemon juice, in Italy and California.

The annual U. S. production of citric acid is in the neighborhood of 10,500,000 pounds.

Vinegar

A dilute alcohol solution seeded with *Bacterium aceti*, after the addition of nutritive solution, causes the formation of acetic acid, provided air has access to the vat. The reaction is:

$$C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O.$$

Wines are used to make vinegars, and furnish the strongest (8 per cent acetic acid) as well as those with the best flavor. Cider which has been fermented is largely used, and furnishes a 4 to 5 per cent vinegar.

The *Bacteria aceti* form films which are called mother of vinegar; the souring may take place in casks, the new stock being seeded by leaving a portion of the finished vinegar to mix with it. The more general process is to pour the new stock down shavings which carry the mothers, while a gentle current of air passes upward.

A very fair amount of acetic acid made by bacterial action is used in the chemical industries, as such, and for the manufacture of ethyl and other acetates; generally the dilute acetic acid may be used.

Ethyl alcohol may be changed into acetic acid by catalytic oxidation at elevated temperatures.

Other Patents

U. S. Patent 1,885,096, process for producing butyl alcohol, acetone, and ethyl alcohol from the same mash; 1,858,808, butyl alcohol and acetone from a mash of waste pulp of a potato flour factory; 1,858,488, propagating yeast in a yeast nutrient solution consisting of a water solution of molasses, urea and in non-ammoniacal inorganic yeast nutrient solutions; 1,766,715, production of lactic acid and its derivatives by fermentation of materials containing carbohydrates; 1,875,536, continuous fermentation process for the production of butyl alcohol; 1,802,163, manufacture of butyl alcohol, by fermenting a mash consisting of molasses, a phosphate, and an addition of malt germs; 1,818,530, continuous manufacture of yeast by the air-fermentation method; 1,380,067 and 1,432,761, chlorine on pentane in presence of activated charcoal and esterification of the amyl chloride at 400° to 450° F. and 250 lbs. pressure; 1,982,160, manufacture of acetic acid from alcohol; U. S. Patent 2,230,318, alcohol production by fermentation; British Patent 523,262 on using bran and cereal germs. U. S. Pat. 2,423,897 describes the fermentation for vinegar in mist droplets kept suspended by turbulent air.

Problems

1. A Cuban molasses has a specific gravity of 1.4, and the analysis given in the text. There are received 100,000 gallons at Baltimore, brought by tankers; this amount is fermented for ethyl alcohol. The conversion is 90 per cent, and the recovery of the alcohol in the beer in the form of industrial alcohol, 94 per cent. Expressed in

[30] U. S. Pat. 1,965,429 and 2,148,874. [31] U. S. Pat. 1,792,657.

pounds of 100 per cent alcohol, how many pounds are collected? If the industrial alcohol is 95 per cent, how many gallons are obtained, the specific gravity being 0.816?

2. The starch contained in one ton of dry corn, with 73 per cent starch, is separated and cooked into a paste. It is then fermented to butyl alcohol and accompanying products as listed in the text. The liquid products are, let us assume, 50 per cent by weight of the starch taken. How many pounds of each are obtained? The parts of the several products are parts by weight.

3. Citric acid anhydrous is made from cane sugar; the acid made is 75 per cent by weight of the sugar taken. Over a period of several days, 10 tons of cane sugar are fermented into opaque anhydrous citric acid. The yield in crystal from acid in the hot liquor is 80 per cent. Find the weight of product.

4. A brewery plans to produce 100 barrels of beer a day. How many fermentation tanks will be required, how many mash tuns and copper boilers? In order to have the proper capacity, what will be the size and number of the various vessels? Let the fermenting vats be square in cross-section, the other vessels circular. It may be assumed that 105 barrels of wort will be required for the intended production.

Reading References

"Seed-culture methods in the production of acetone and butyl alcohol by a fermentation process," Horace B. Speakman, *J. Ind. Eng. Chem.*, 12, 581 (1920).

"Butanol and acetone from corn," D. H. Killeffer, *Ind. Eng. Chem.*, 19, 46 (1927).

"Acetone," Lloyd C. Cooley, *Ind. Eng. Chem.*, 29, 1399 (1937).

"Ethyl alcohol," A. A. Backus, p. 1151; "Lactic acid," J. F. Garrett, p. 1153; "History and development of the modern yeast industry," Charles N. Frey; "Development of butyl-acetonic fermentation industry," C. L. Gabriel and F. M. Crawford, p. 1163; "Some minor industrial fermentations," O. E. May and H. T. Herrick, p. 1172; "The chemical approach to problems of fermentation," Ellis I. Fulmer, p. 1148; *Ind. Eng. Chem.*, 22 (1930).

"Butanol fermentation process," C. L. Gabriel, *Ind. Eng. Chem.*, 20, 1063 (1928).

"Enzymes," J. B. S. Haldane, London and New York, Longmans, Green and Co., 1930.

"Mechanism of enzyme action," F. F. Nord, Baltimore, Williams and Wilkins Co., 1929.

"Chemistry and certain problems of applied mycology," Hubert Martin, *J. Soc. Chem. Ind.*, 49, 11T (1930).

"Discussion on micro-organisms and their application to industry and research," a symposium, *Trans. Soc. Chem. Ind. (British)*, 42, 169T-180T (1923).

"Process economies in the alcohol industry," Gustave T. Reich, *Chem. Met. Eng.*, 44, 131 (1937).

"Silver in the artificial aging of brandies," E. Arthur Beavens, Harry E. Gorseline, and E. K. Nelson, *Ind. Eng. Chem.*, 29, 623 (1937).

"Alcohol from farm products," P. Burke Jacobs, *Ind. Eng. Chem.*, 31, 162 (1939).

"Brewing: Science and Practice," Volume II, "Brewing processes," H. Lloyd Hind, New York, John Wiley and Sons, 1940.

"Distilling beverages from grain," G. T. Reich, *Chem. Met. Eng.*, 40, 618 (1933).

"Design of a modern molasses distillery," G. T. Reich, *Chem. Met. Eng.*, 41, 64 (1934).

"Industrial Microbiology," S. C. Prescott and C. G. Dunn, New York, McGraw-Hill Book Company, 1940.

"The development and design of a continuous cooking and mashing system for cereal grains," E. D. Unger, H. F. Wilkie and H. C. Blankmeyer, *Trans. Am. Inst. Chem. Eng.*, 40, 421 (1944).

"Alcohol from agricultural commodities," P. Burke Jacobs, AIC-95, Northern Regional Research Laboratory, Peoria, Ill., May, 1945.

"Miscellaneous publication 327, Motor fuels from farm products," P. Burke Jacobs and Harry P. Newton, 129 pages, U. S. Dept. Agriculture, 1938.

In Press: "Industrial alcohol, its production and use in relation to agriculture," P. Burke Jacobs, Northern Regional Research Laboratory, U. S. Dept. Agriculture (1949).

In a democracy, it is necessary to disseminate news readily and cheaply; one of the indispensable agencies in that process is an abundant supply of paper. For the transfer of knowledge from generation to generation, hence for the preservation of knowledge, paper is required. This material is therefore not only a convenience, but one of the cornerstones of our civilization.

Chapter 21

Cellulose from Wood; Pulp and Paper*

The importance of the pulp and paper industry in the field of industrial chemistry can be comprehended from the single statement that the per capita consumption of paper in the United States within recent years has exceeded 300 pounds per year.

An idea of the rate of development of the industry can be obtained by contrasting this per capita requirement with that for several selected years, because, for the most part, with perhaps the exception of newsprint production, facilities for papermaking in the United States up until World War II increased only slightly more rapidly than consumption. (Expansion of production facilities during and since World War II has gradually closed the gap between demand and supply.) Newsprint capacity, on the other hand, has fallen far behind requirements as developed during the past quarter century. The annual per capita paper consumption figures for selected years follow:

Year	Pounds Consumed Per Capita
1810	1
1819	2
1869	20
1899	57
1914	112
1929	220
1947	344

The invested capital in the pulp and paper industry of the United States is estimated at over three and a half billion dollars. This capital structure, according to figures for 1948, is spread over 558 firms which operate 239 pulp mills and 756 paper mills. The pulp mills are distributed over 24 states; the paper mills over 37 states and the District of Columbia. Most of the pulp mills are integrated with paper mills; a few are not. Some of the pulp mills not integrated with paper mills are owned by paper mill organizations and serve as sources of pulp supply for paper mills operated by them. Sometimes more than one kind of pulp mill is combined with a paper mill into a single operation. Newsprint, for example, usually is made in a mill which also produces sulfite pulp and groundwood pulp, these two kinds of pulp being commonly combined to make newsprint.

Based on tonnage, Washington, Maine, Louisiana, Wisconsin, and Florida, in the order given, were the five most important pulp-producing

* In collaboration with Harry E. Weston, Associate Secretary-Treasurer, The American Pulp and Paper Mill Superintendents Association, Inc. (formerly Editorial Director, *The Paper Industry and Paper World*).

states in 1946. New York, Michigan, Ohio, Wisconsin and Pennsylvania, in the order given, were the states of greatest paper tonnage during 1946.

To produce these tremendous tonnages of pulp and paper requires numerous raw materials. For purposes of easy classification, these materials may be broadly divided into two groups, namely, fibrous and non-fibrous. The more important fibrous raw materials are wood, waste paper, cotton

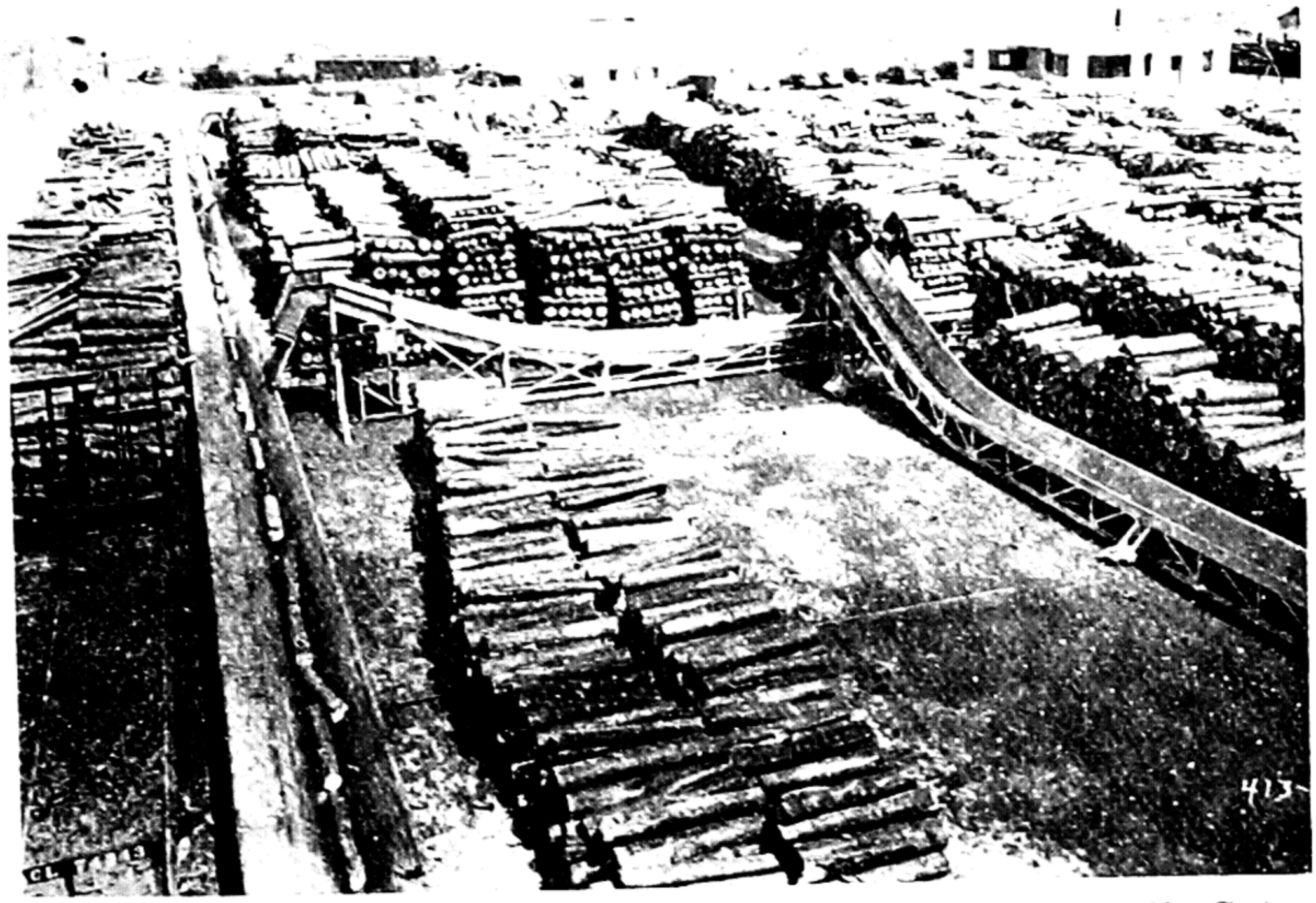


FIGURE 159.—Pulpwood in storage in mill yard. (Courtesy of Jeffrey Mfg. Co.)

and linen rags—both old and new—straw, old rope, and cotton linters; the non-fibrous are lime, silicate of soda, salt cake, sulfur, limestone, chlorine, clay, alum, rosin, soda ash and caustic soda.

Published statistical data reveal that the following wood species, in the order given, accounted for nearly 90 per cent of the quantity of pulpwood consumed by United States mills in 1944: pine, spruce and fir, hemlock, aspen, chestnut, and yellow poplar. The total consumption of pulpwood that year by these same mills amounted to 16,757,400 cords.

TABLE 67.—*U. S. wood pulp consumption by regions (1946).*

(Cords of 128 cubic feet-rough wood basis)

Region	Softwood	Hardwood	Total
Northeast	2,917,986	546,870	3,464,856
Appalachian	582,357	918,142	1,500,499
Lake States	2,051,017	503,017	2,554,034
South	7,052,424	465,355	7,517,779
Pacific Northwest	2,780,392		2,780,392
Totals	15,384,176	2,433,384	17,817,560

For the most part, this huge quantity of wood is reduced to pulp by one of four processes, a fifth process being employed to a more limited extent. The four major pulping processes are designated as groundwood or mechanical, sulfite, soda, and sulfate; the fifth process, as semi-chemical. The groundwood or mechanical pulp process, as its name indicates, is strictly mechanical in character; the sulfite, soda, sulfate, and semi-chemical processes are chemical in nature; the sulfite process employs an acid liquor in pulping; the soda process, an alkaline liquor; the sulfate process, an alkaline liquor; and the semi-chemical process, a neutral liquor, or some variation in alkaline pulping procedure.

TABLE 68.—*U. S. wood pulp production by kinds (1946).*

Kind	Quantity in short tons
Mechanical	1,811,622
Sulfite	2,476,468
Sulfate	4,588,016
Soda	476,211
Defibrated, exploded Asplund fiber, etc.	761,544
Semichemical screenings damaged, and all other	492,666
U. S. Total	10,606,527

Wood Preparation. To convert wood into pulp by any of the pulpmaking processes, it first is necessary to remove its bark, and, in the case of chemical pulp, to reduce the barked wood into small chips of fairly uniform size. The nature of the operations for doing this work depend somewhat on the relative sizes of the wood being pulped, the method or methods employed in getting the wood to the mill, and the kind and quality of pulp being produced by the mill.

Although there are a number of different designs of machines employed for removing bark from pulpwood, probably the barking drum is the most common. This machine consists of a cylinder-like drum, sometimes as much as 12 feet in diameter and 45 feet long, positioned horizontally and sometimes incompletely partitioned into several sections, that is, made of special-shaped, longitudinally placed steel sections, individually spaced to permit the bark from the wood to pass between them. In operation, this drum is revolved slowly, only a few revolutions per minute; the wood, cut to a uniform length (commonly not exceeding five feet), enters continuously at one end, tumbles around within the drum, and discharges from it continuously at the other end, the bark being removed by the tumbling of the various short sections of wood against one another in their passage through the drum. Water also is used in the operation to free the barked wood of any loose bark that otherwise might adhere to it.

The capacity of equipment of this kind is influenced largely by the species of wood being barked and by the condition of the wood at the time of barking. A barking drum with a diameter of 10 feet and a length of 30 feet, for example, might handle four to five cords of dry, frozen spruce pulpwood per hour, as contrasted with 10 to 20 cords per hour if the wood is river-driven.

The barked wood, without any further preliminary treatment, is ready for reduction to mechanical pulp. To make it ready for treatment by any of the chemical pulp-making processes, however, it must be further reduced to chips, which approximate from one-half to one inch long and from one-eighth to three-sixteenths inch thick.

The chipping is accomplished in a machine known as a chipper, which gives to the wood, as it passes through the machine lengthwise, a slicing cut at an angle of about 45 degrees. This type of cut allows the natural pores

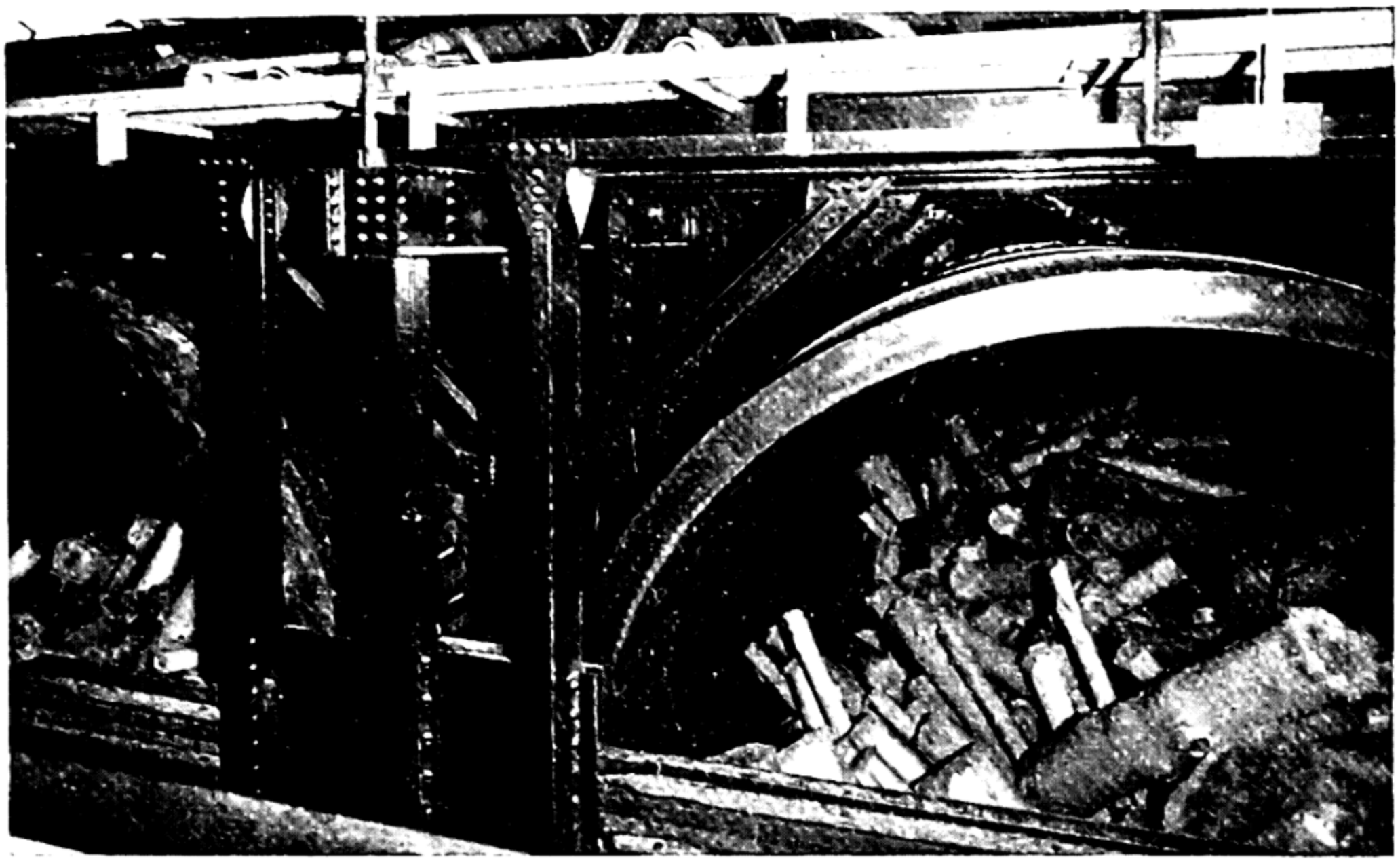


FIGURE 160.—Wood being barked by two barking drums. (Courtesy of Chicago Bridge & Iron Co.)

of the wood to remain open and at the same time presents a much greater penetration surface to the action of the pulping chemicals, penetration taking place mainly through the ends rather than on the flat side of the chips.

The chipper consists essentially of a hooded, heavy circular disc, made of close-grained cast iron or heavy steel plate, slotted for and equipped with three or more knives (as many as 8 or 10 on some of the newer units), and positioned vertically on a horizontal shaft, together with a cast-iron spout so placed in relation to the face of the disc that it directs the wood against it and to the cutting edge of the knives at the proper cutting angle. A common size of four-knife chipper has a disc 84 inches in diameter and a capacity of about 10 cords per hour. The largest wood chipper ever built, so far as is known, has a disc 171 inches in diameter. Installed in a Pacific Coast mill during 1941, this chipper is designed for handling wood up to 40 inches in diameter, has a rated capacity of about 145 cords per hour, and is equipped with a 1000 hp. motor.

Practical uniformity in chip size is important in the successful digestion or cooking of the wood. Therefore, the chips produced by the chipper are

screened to separate those of desirable size from oversize material and sawdust. The oversize material is crushed or reduced in size and re-screened; the sawdust is frequently utilized for fuel.

Several designs of chip screens are in common use. They include such types as revolving or rotary, shaker or reciprocating, vibrating, and oscillating. The revolving screen commonly consists of a single or double cylinder arrangement, the screening surface depending upon the design. Although the shaker, vibrating and oscillating units may vary somewhat in detail, the primary difference of the several designs is in the method of imparting screening action to the tables.

Liquor Preparation. Roughly speaking, about 2,000 gallons of cooking liquor are required per ton of chemical pulp. This requirement necessitates

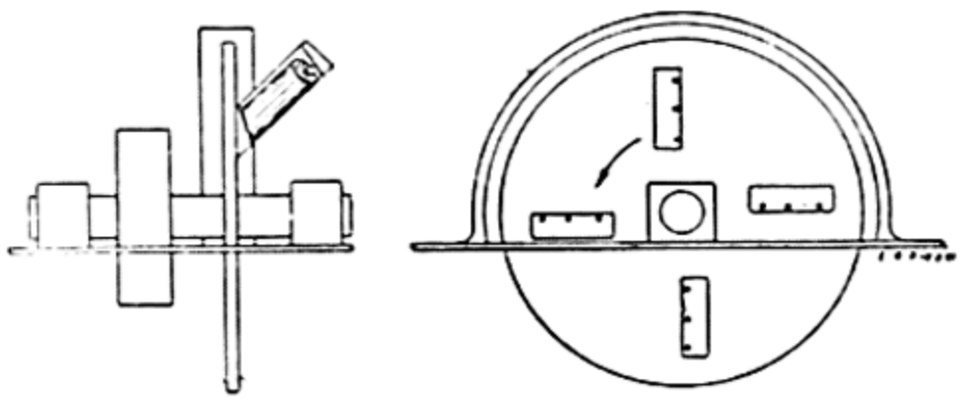


FIGURE 161.—Wood chipper.

an extensive layout of equipment for use in producing such liquor in every sulfite, soda, and sulfate mill. In the case of the sulfite mill, the equipment is grouped together in a portion of the mill designated as the acid plant; the combination of equipment for liquor preparation in a soda or a sulfate mill is known as the chemical recovery plant.

Sulfur (or a source of sulfur such as iron pyrites), limestone or lime, and water are the chemical raw materials needed in the preparation of sulfite cooking liquor. The sulfur is burned, or the pyrites roasted, to produce sulfur dioxide gas. Since sulfur is so readily available to United States mills, it is the common raw material used for producing the gas. In burning the sulfur, it is necessary to control both the temperature of burning and the quantity of air supplied for it. The usual temperature range for the gas, just previous to being cooled, the next operation in the cycle, probably is from 700-1000° C. Theoretically, one pound of oxygen, the quantity contained in about 54 cubic feet of air, is required to convert one pound of sulfur into two pounds of sulfur dioxide gas. Somewhat more air than the theoretical amount is required in practice.

Cooling of the gas is essential to its absorption in water. Rapid cooling is necessary to minimize the production of sulfur trioxide. Absorption of the gas in water is carried out in the presence of lime (as milk-of-lime) or of limestone. In either case, the result is the same, namely: a bisulfite of the base containing an excess of sulfurous acid. To this liquor, which is designated as raw acid, is added sulfur dioxide gas relieved from the digesters during the cooking cycle to obtain the cooking acid of the process.

In brief, therefore, the major equipment of an acid plant used to produce cooking acid for a sulfite mill would include one or more sulfur burners and a combustion chamber arrangement, a gas cooler (water being used as

the coolant), absorption apparatus, and equipment to permit the use of digester relief gas for strengthening of the raw acid. In the latter case, the relief gas and the raw acid may be brought together in an accumulator, a rather recent but widely accepted development which makes possible the use of a hot and stronger acid in charging a digester; or it may include a gas cooler (also using water as a coolant) and a recovery tower.

Sodium carbonate, lime and water are the raw materials commonly used in the production of the cooking liquor of the soda process. This liquor, primarily a solution of caustic soda, with a strength of 8° to 15° Bé. at 60° F., is made by causticizing a solution of soda ash with quick lime. The

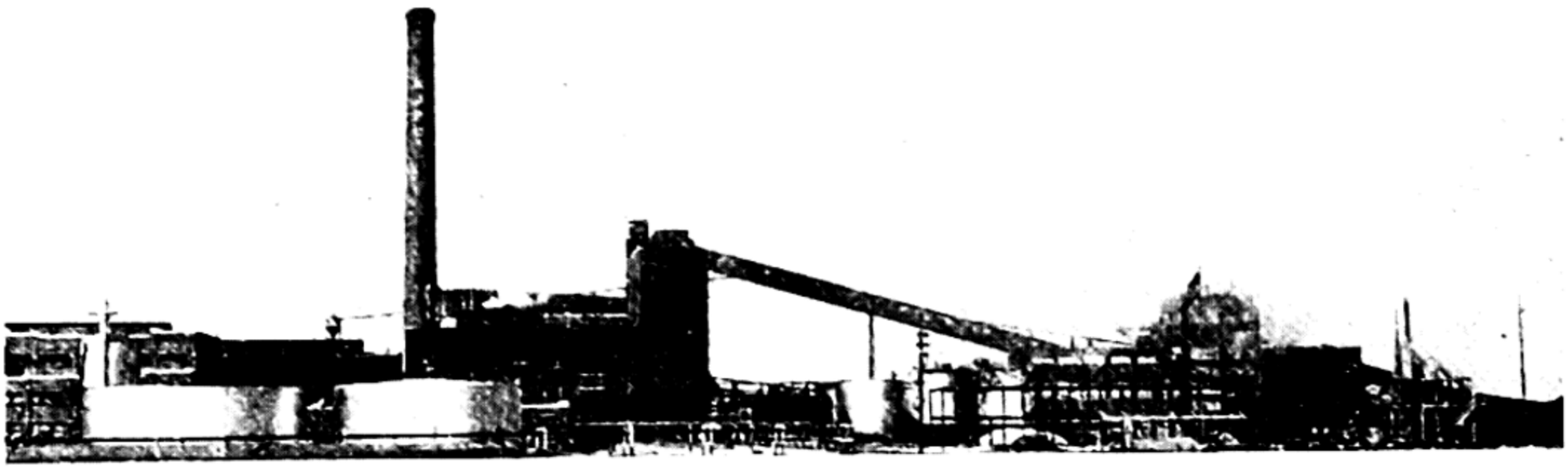


FIGURE 162.—General view of modern pulp and paper mill. (Courtesy of Chicago Bridge & Iron Co.)

causticizing reaction produces not only the caustic liquor but also a precipitate of calcium carbonate. This precipitate is settled out or filtered from the caustic liquor. By far the larger part of the soda ash required for the reaction, from 80 to 85 per cent, is obtained from cooking liquor which already has been employed for pulping. Only enough replacement soda ash has to be used to make up for losses which occur in the cycle of mill operations.

The liquor of a digester charge following cooking, designated as black liquor, is obtained for alkali recovery through the pulp washing operation, an operation essential in the making of soda pulp fiber suitable for use in papermaking. This liquor, diluted tremendously by the washing operation, not only contains nearly all of the alkali of the original liquor, but also about half the weight of the wood of the digester charge. It is common practice in making this alkali available for reuse to first concentrate the liquor to about 35° Bé. and then to pass it through an incinerator from which it is discharged as a very hot cinder, known as black ash, and consisting largely of a mixture of sodium carbonate and carbon. Constituting about 65 to 80 per cent of the weight of the black ash, the sodium carbonate portion is leached free of the carbon, thus making it available for causticizing with lime.

A chemical recovery plant of a soda pulp mill, therefore, consists essentially of an evaporator and incinerator installation for making the alkali in the black liquor available for re-use as sodium carbonate, an installation

of leaching tanks to free the sodium carbonate in the black ash from the carbon also contained in it, and a causticizing plant to convert the sodium carbonate into caustic soda.

The raw materials used in the production of sulfate cooking liquor are sodium sulfate, lime, and water. In the preparation of this liquor, like that of the soda process, use is made of the cooking liquor from previous pulping operations. This liquor, also designated as black liquor just as in the soda process, likewise is concentrated by evaporation following the pulp-washing operation. The concentrated liquor then may be handled in one of two ways. The older process involves the formation of black ash as in the soda process, mixing this ash with the quantity of sodium sulfate necessary to make up for the loss of alkali, feeding this mixture into a smelting furnace (the carbon in the ash serving as a source of fuel), where the sodium sulfate is reduced to sodium sulfide and the sodium carbonate of the ash is freed of the carbon by the burning operation, and then causticizing with quick lime the smelt that issues from the furnace, thus producing a cooking liquor consisting largely of caustic soda and sodium sulfide, and a precipitate of calcium carbonate. The newer method, in part, involves mixing the sodium sulfate with concentrated black liquor, and feeding this mixture into a chemical recovery unit, which combines a smelting furnace and a steam boiler. Here, the carbon of the liquor serving as the source of fuel, the sodium sulfate is reduced to sodium sulfide, and steam is produced for power and process use. The smelt issuing from such a unit, as in the case of the older smelting furnace, consists essentially of a similar mixture of sodium carbonate and sodium sulfide, which when causticized produces the cooking liquor of the process and a precipitate of calcium carbonate. The calcium carbonate precipitate, commonly designated as lime sludge, may be calcined and the lime so produced used in part as a source of lime for causticizing.

Therefore, equipment essential to the production of sulfate cooking liquor would include an evaporator installation, and, depending upon the method of sodium sulfate reduction, a rotary incinerator and smelting furnace combination, or a chemical recovery unit with steam boiler arrangement, together with necessary equipment for causticizing and possibly a lime kiln for calcining the sludge.

The semi-chemical process does not delignify the wood to the extent of any of the previously mentioned chemical processes. It merely softens the chips, which are then reduced to pulp mechanically. Pulp yields by this process, which commonly employs a neutral sodium sulfite liquor for cooking, range from 70 to 80 per cent of the weight of the wood. One notable use of the process is in the utilization of tannin-extracted chestnut chips in the production of stock for corrugating board.

Pulping Wood Mechanically. A machine designated as a grinder is used to reduce the barked wood to mechanical pulp. Within recent years, considerable development in grinder design has taken place; so that the grinders now in use may be classified broadly into one of three types—pocket, magazine, and pocket-magazine combination. Whatever the design, the

grinder includes a cylinder-like pulpstone (either natural or manufactured) positioned on a horizontal shaft and a means for forcing the barked wood against its face during operation. The wood always is placed lengthwise across the pulpstone face, so that as the stone revolves, the wood fibers are separated from one another in their lengthwise direction. Sufficient water is used in the grinding operation both to prevent burning of the wood and to serve as a vehicle for carrying the pulp fiber away from the machine.

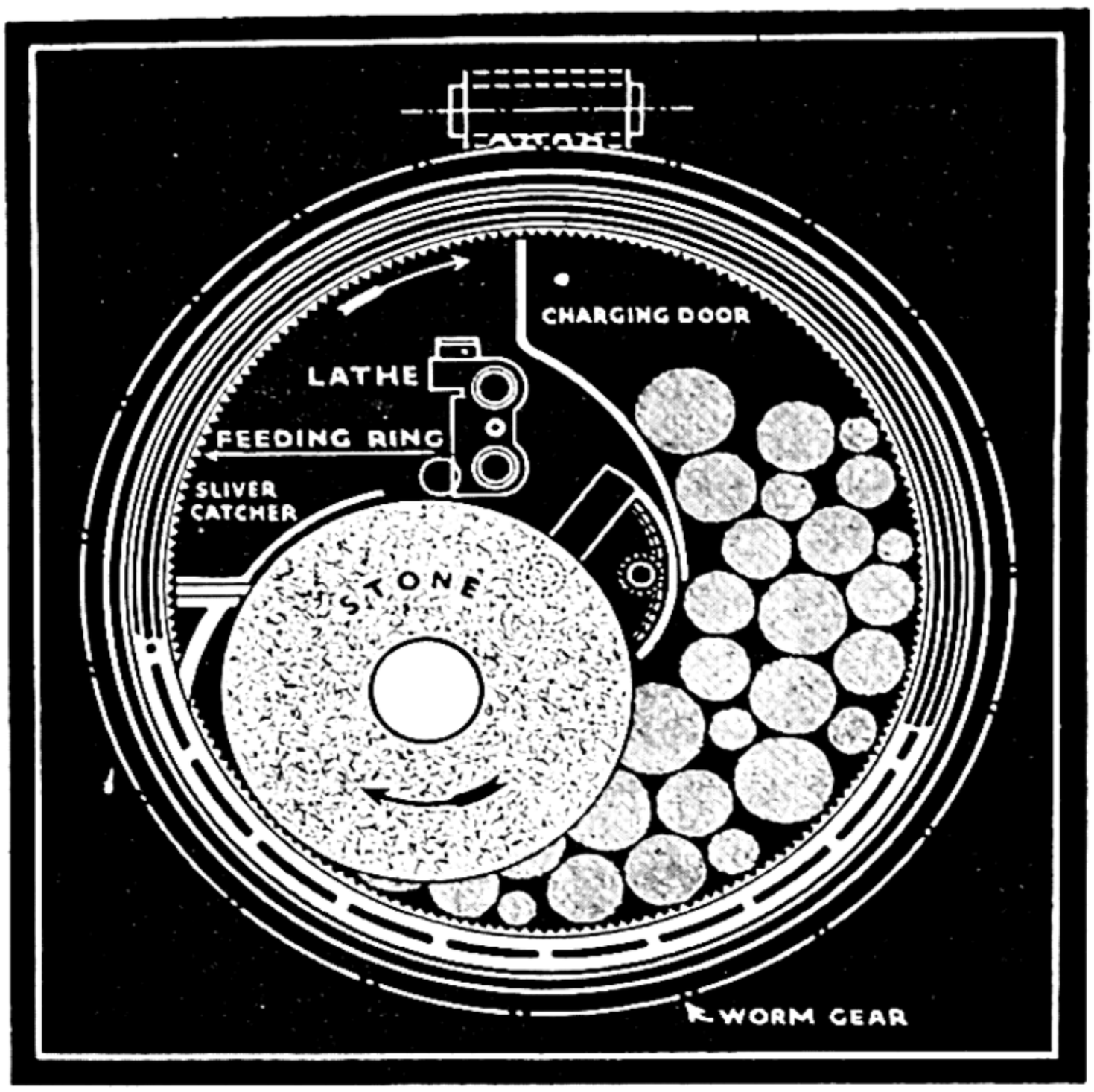


FIGURE 163.—Elevation Sketch of a Recently Developed Woodpulp Grinder Showing Principles of Operation. (Courtesy of The Appleton Machine Co.)

In the case of the pocket grinder, wood is fed intermittently into one of several chambers or pockets, located radially along the upper half of the periphery of the pulpstone, and there forced against the pulpstone face by means of a hydraulically operated piston arrangement. The older type of magazine grinder makes use of two vertically positioned, wood-charging magazines in relation to the pulpstone and an intermittently and automatically operated pocket-type feeding arrangement for each magazine. This design was followed by a single vertically positioned magazine directly over the pulpstone, so designed as to force the wood continuously against its face. The most recently developed magazine grinder employs a large cast-iron ring so mounted eccentrically around the pulpstone and within a cast-iron housing that the ring almost contacts the stone at a point about 210° from the vertical. Such a positioning of the stone in relation to the ring leaves a relatively small space on one side of the stone and a large

crescent-shaped area on the other side. A baffle, built into the smaller area, functions as a sliver pocket; the crescent-shaped space, also utilizing a baffle arrangement, serves as the loading pocket for the wood. With the rotation of both the ring and the stone, both in the same direction, the stone at a constant speed of approximately 240 rpm., the ring at a speed varied to the operating pressure desired, a charge of wood, usually about one-half cord, is reduced to pulp.

TABLE 69.—*U. S. woodpulp production by states (1946).*

State	Quantity in short tons	State	Quantity in short tons
Washington	1,332,940	New Hampshire	177,434
Maine	1,185,232	New Jersey	62,700
Louisiana	989,366	California	13,692
Wisconsin	889,139	North Carolina and South Carolina	923,926
Florida	694,594	Maryland and Virginia	647,172
New York	555,847	Tennessee and Alabama	455,837
Mississippi	463,456	Arkansas and Texas	426,411
Georgia	422,648	Ohio, Illinois and Iowa	88,911
Oregon	406,716	Vermont, Massachusetts and Rhode Island	59,430
Minnesota	318,605		
Pennsylvania	272,598	U. S. Total	10,606,527
Michigan	219,873		

The pocket-magazine combination type of grinder makes use of two pockets and two magazines. Each pocket, one on either side of the stone face, positioned somewhat nearer the horizontal than in the older types of pocket grinders, carries a magazine in its top to permit ready charging with wood.

Among the more important operating factors to be considered in the grinding of wood for mechanical pulp are: condition of pulpstone surface, speed of stone, operating pressure, temperature of grinding, and the physical condition and species of wood being ground.

Chemical Reduction of Wood to Fiber. Digesters used for cooking wood chips with acid or alkali are usually vertically-positioned cylindrical pressure vessels of steel plate construction. The sulfite digester commonly is larger than either the soda or sulfate digester. It also is lined with acid-resisting brick while generally no lining is required for digesters used in alkaline pulping. A sulfite digester with a diameter of 15 feet, a height of 50 feet, and a lining 10 inches thick will hold approximately 22 cords of wood per charge.

The yield of fiber from a digester charge is dependent upon a number of factors. Among the more important of these factors would be the specific gravity or density of the wood, the strength of the cooking liquor, the temperature and pressure of the cooking cycle, and the time interval or length of cook. In general, it will average a little less than 50 per cent.

Although in some instances steam is introduced directly into a digester charge, modern practice favors external heating and forced circulation of the cooking liquor. When a forced circulation system is employed, the

liquor may be heated indirectly through the use of a heat exchanger or directly through the incorporation of a special type of heating unit into the circulating system.

There is no standard procedure for the handling of a digester charge. Practice varies with the individual mill. Probably a typical sulfite cooking procedure for an easy bleaching pulp would be somewhat as follows: (1) Bring digester to cooking pressure of 75 pounds in two hours. (2) Increase digester temperature gradually to about 150° C. (302° F.). Maintain pressure at 75 pounds by relieving gas pressure on charge. Time interval about 10 hours from initial steaming. (3) Shut off steam supply. Continue relieving for one hour to bring pressure down to 50 pounds. (4) Discharge digester contents at 50 pounds pressure.

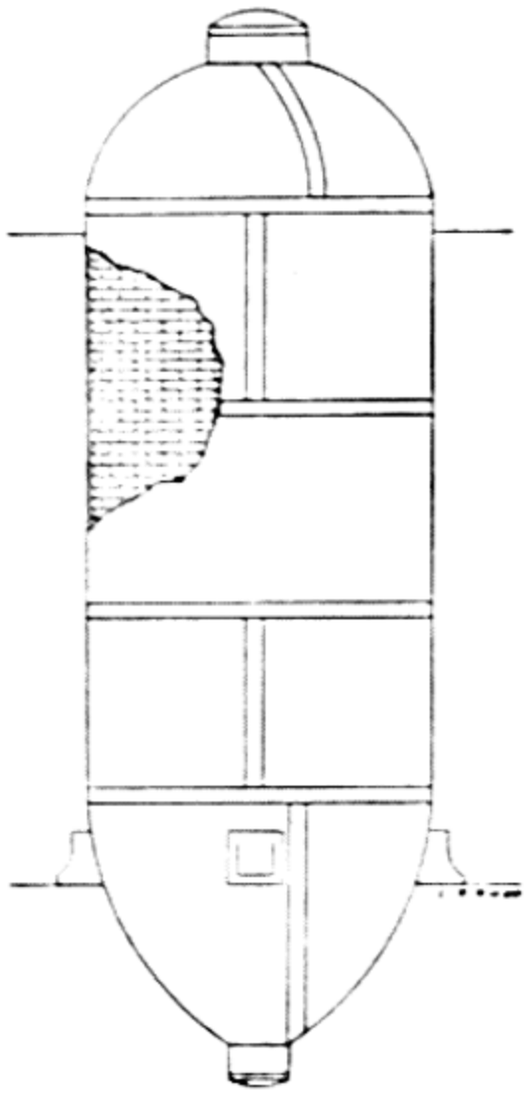


FIGURE 164.—Digester for sulfite pulp.

It is common practice in both soda and sulfate cooking procedures to reach cooking pressure as soon as possible and to maintain the charge at this pressure to the end of the cook. Likewise, higher operating pressures and shorter cooking cycles are used than in sulfite. Usual practice employs a pressure of 100-110 pounds and a cooking cycle of three to six hours.

Washing Chemical Pulp. With the cooking operation completed, the digester contents are discharged under pressure into a specially designed tank which permits rapid removal of the blow steam to the atmosphere, or, in the case of some of the newer sulfate mills, to a condenser. If a blowdown condenser is used, it furnishes hot water for use in pulp washing, the immediate operation to follow.

The tank used for receiving the digester charge and for pulp-washing in a sulfite mill is designated as a blowpit. It is commonly of wood construction, making use of a vertical stack for removal of blow steam to the atmosphere and a false bottom for washing the pulp free of the spent liquor of the operation.

This liquor, commonly designated as waste sulfite liquor, has commanded the attention of numerous research workers. Commonly, it is discharged into the stream or other body of water upon which a mill is located, and as a result, pollution of the water has become an acute problem in a number of sulfite mill communities. Up to the present, most mills do not utilize this liquor in any way because of their inability to do it economically.

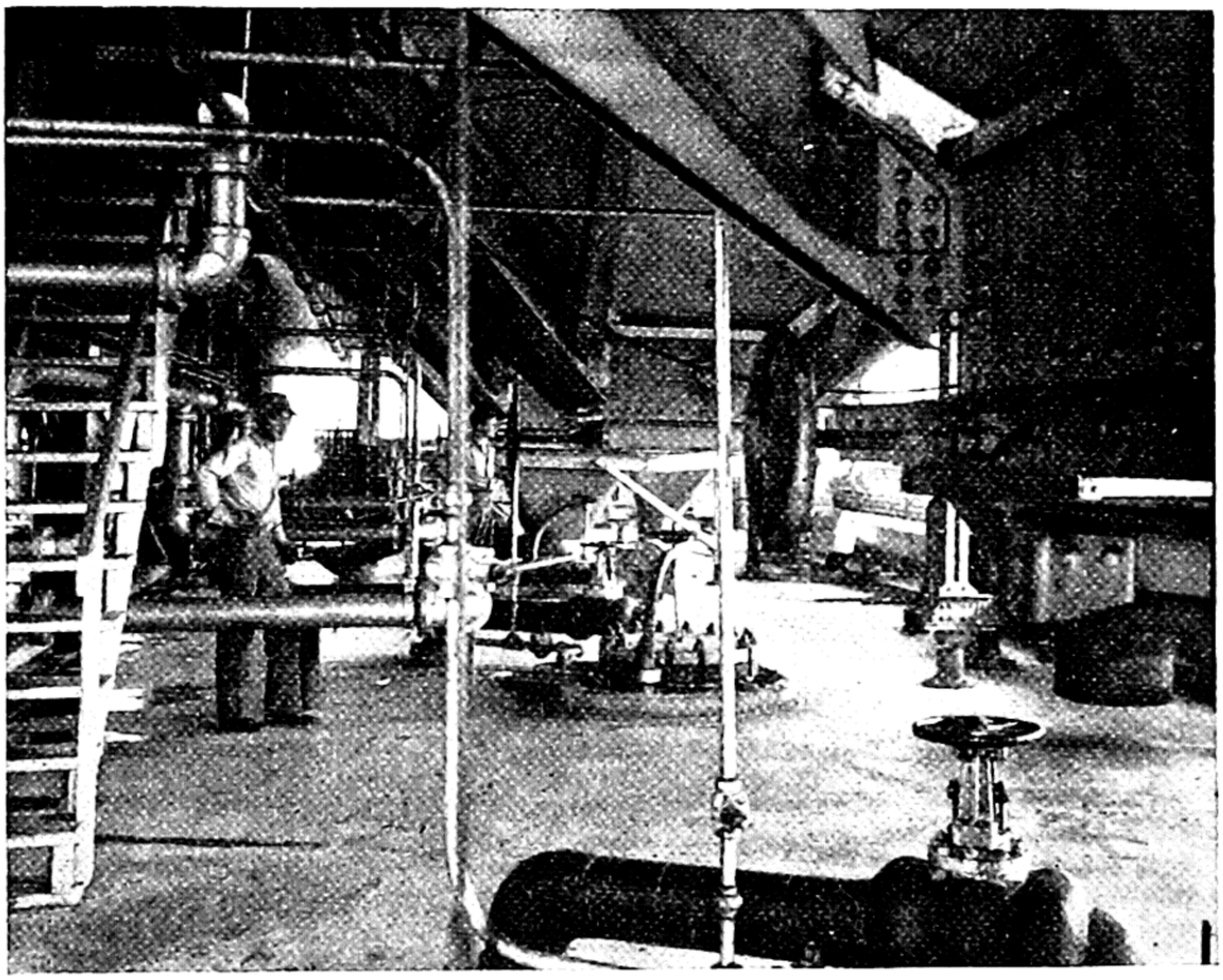


FIGURE 165.—Operating floor in digester house of sulfate pulp mill. (Courtesy of *Paper Industry and Paper World.*)

However, in a few instances, it is being used as a road binder, tanning material, and as a source of fuel, as well as in the production of vanillin, alcohol, plastics, yeast, and other products.

In a soda or sulfate mill, a tank, known as a cyclone or blow tank, may be used to receive the digester charge and to exhaust the blow steam, the pulp stock and black liquor of the charge being discharged from it by gravity, as desired, into one of a series of wash tanks or pits; or the charge may be blown directly into one of a series of tanks, known as diffusers, which serves in the same way as the blowpit of the sulfite mill.

Screening the Pulp Fiber. After the washing operation is completed, large quantities of water being used for the purpose, the chemical pulp fibers are ready for screening. A similar screening procedure is required of groundwood pulp as it issues from the grinder; but, in producing groundwood pulp, no washing operation, as practiced in making chemical pulp, is required. The purpose of the screening operation is twofold: first, to remove slivers and small unground slabs from groundwood pulp as it issues from

the grinder pit, and to remove knots and other partially cooked chips from the washed chemical pulp; and secondly, to separate the main mass of fibers into two or more grades depending primarily upon variation in diameter. The screening procedure, therefore, is commonly divided into two operations—coarse screening and fine screening.

Coarse screening of groundwood pulp is accomplished by the use of a machine called a sliver screen; the machine employed for the coarse screening of chemical pulp fiber is known as a knotter. There are a number of different designs of machines for performing this coarse screening operation. In some instances, the machine is designed to handle either groundwood or chemical pulp; in other instances, just one or the other. One design of coarse screen, adapted to either groundwood or chemical pulp fiber, with a screening cylinder 5 feet in diameter and 12 feet long and with $\frac{3}{16}$-inch diameter perforations in the screen plates constituting the cylinder, has a capacity of 100 tons of mechanical pulp or 50 tons of chemical pulp per 24 hours. The same machine with $\frac{1}{4}$-inch perforations in the screen plates will handle 125 tons of mechanical pulp or 65 tons of chemical pulp per 24 hours.

In this machine, the slivers and screenings, also called tailings, are freed of good fibers as they travel from the inlet end of the screen to the tailings discharge at the opposite end. A spiral within the screening cylinder retards the movement of the slivers and screenings in their passage through the machine and forces them to travel nearly 100 feet before being discharged. Accepted fiber, on the other hand, passes through the screen plate perforations into a pit or vat from which it is delivered to the fine screen installation.

In general, fine screens may be classified into one or two types, either diaphragm (flat), or centrifugal. The diaphragm or flat screen depends for its operation upon both gravity flow and suction or vibration; centrifugal force is utilized in the operation of a centrifugal screen.

The diaphragm screen is characterized by a series of slotted metal plates positioned near the bottom of a comparatively shallow box or vat of wood or metal construction; below this, forming the bottom of the vat, is a series of diaphragms, which, when actuated, serve to draw the accepted fiber through the slots in the plates. The width of slots in a given plate is dependent upon the kind of pulp being screened and upon the kind of job required of the screen installation. A modern 12-plate screen, with plates 12 by 43 inches, will have a capacity of approximately 6 to 11 tons of pulp fiber per 24 hours.

The centrifugal screen consists of an impeller surrounded by an assembly of screen plates which in turn is surrounded by the machine casing. Positioned either horizontally or vertically, the impeller, when in operation, forces the stock being screened against the screen plates, the accepted stock passing through the perforations in the plates to the area within the casing; from this it is discharged, the tailings passing from within the screen plate area to a secondary or tailings screen for a final separation of acceptable fiber from the rejects. The perforated openings in the screen plates, depend-

ing upon the make of screen and the service, usually range from 0.055 to 0.01 inch in diameter.

Both diaphragm and centrifugal screens are designed for continuous operation on a very dilute suspension of fibers. Screened stock generally has a consistency of only 0.25 to 0.60 per cent.

De-Watering or Thickening the Stock. Because of the low consistency of screened stock, a de-watering or thickening operation must follow screening. This operation is necessary whether the pulp is to be used immediately in the succeeding operations or whether it is to be stored or shipped. The desired concentration of pulp fibers determines the type of machine to be employed for thickening. If a consistency of only 3 to 6 per cent is desired, the machine may consist of a vat for receiving the screened stock; a rotating cylinder, with a wire cloth facing, which is suspended in the vat; and some means for removing the fiber mat which forms over the facing wire of the cylinder as it revolves in the stock. Such a machine commonly is called a decker. If a consistency of 15 to 25 per cent or more is desired, a vacuum filter, such as is common to the chemical industries, may be employed.

When a consistency of 30 to 45 per cent is desired, a machine known as a wet machine is used. A wet machine is somewhat similar to a decker, but in addition it includes a press arrangement which delivers the pulp from the machine as a sheet rather than as slush stock. To reduce screened stock to a consistency of 75 to 85 per cent requires a pulp-drying machine. Such a machine is very similar to a papermaking machine in all its essential operating details. In some cases, it actually may be a reinstalled paper machine.

Wood Pulp Bleaching. The bleaching of wood pulp (groundwood, sulfite, soda, or sulfate) has for its object the production of a whiter and a brighter stock. In the case of groundwood, a pulp which contains nearly all of the constituents of the raw wood from which it was produced, except perhaps for a small amount of water-soluble or hydrolyzable material, the process is designed primarily to improve the natural color of the wood, discolored by atmospheric conditions or bacterial decomposition; to improve the color of pulp, discolored somewhat by a high grinding temperature; and to brighten the color of pulp containing metallic compounds, such as iron tannates. Chemical pulp bleaching, on the other hand, is an operation involving the purification of cellulose fiber by removing ligneous material as well as other residues in the pulp.

Several different reducing agents are used for brightening the color of groundwood pulp. Dilute solutions of calcium or sodium bisulfite can be applied to the pulp as it is being thickened on a wet machine, or small quantities of zinc hydrosulfite can be added continuously to the pulp stream by means of a dry feeder, or weighed amounts can be added to the stock in the batch mixer or beater. Sodium peroxide and hydrogen peroxide also have found rather extensive application for the bleaching of groundwood within the past few years.

For many years, a solution of calcium hypochlorite was the only agent commonly used for the bleaching of sulfite and soda pulps. This liquor

was prepared by mixing bleaching powder with water, and then, after a settling period, drawing off the clear, supernatant liquid. This practice, within recent years, has given way to the use of liquid chlorine and milk-of-lime. The first commercial installation in the United States in which

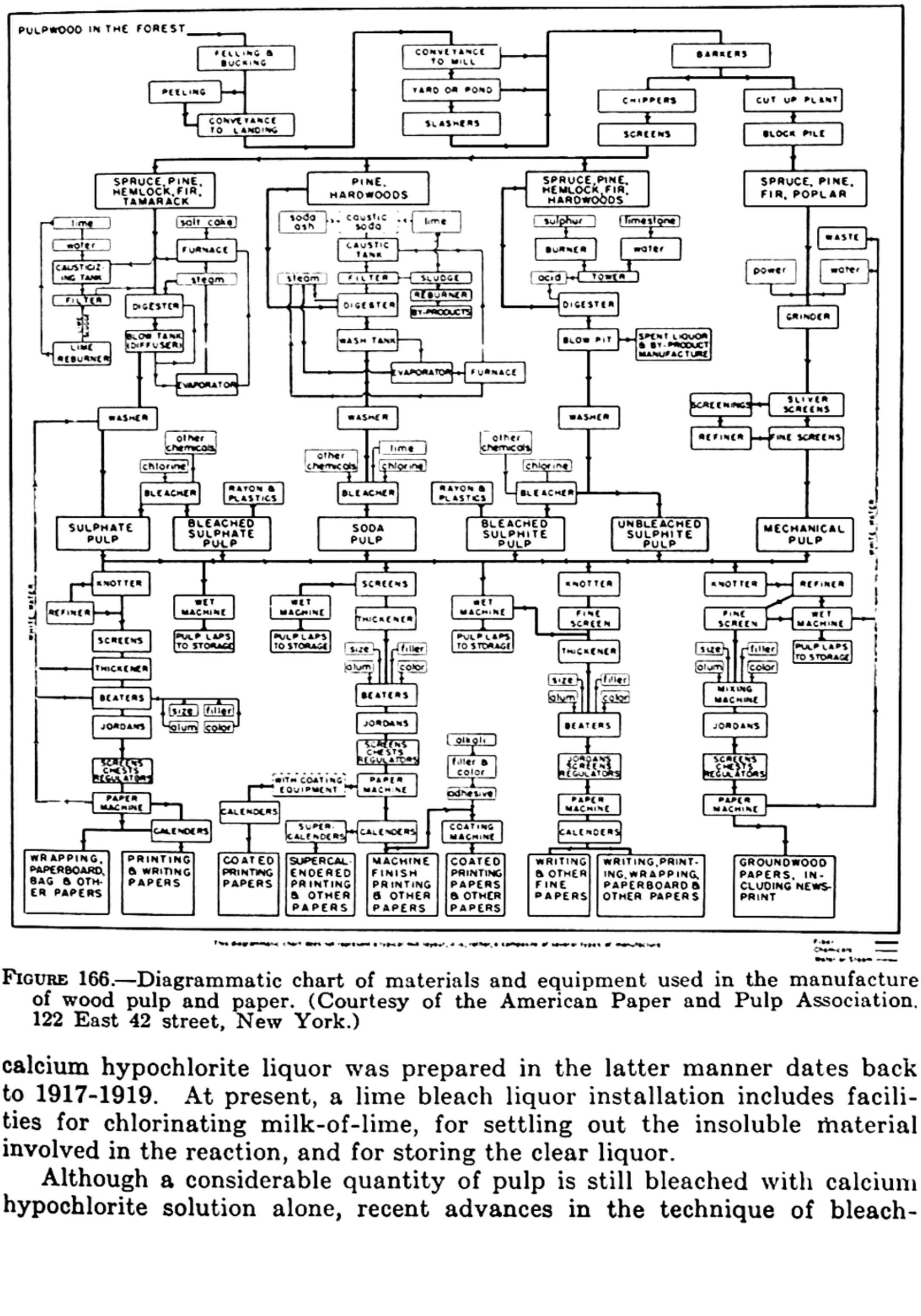


FIGURE 166.—Diagrammatic chart of materials and equipment used in the manufacture of wood pulp and paper. (Courtesy of the American Paper and Pulp Association, 122 East 42 street, New York.)

calcium hypochlorite liquor was prepared in the latter manner dates back to 1917-1919. At present, a lime bleach liquor installation includes facilities for chlorinating milk-of-lime, for settling out the insoluble material involved in the reaction, and for storing the clear liquor.

Although a considerable quantity of pulp is still bleached with calcium hypochlorite solution alone, recent advances in the technique of bleach-

ing make use of it along with direct chlorination, and also sometimes with other chemical treatment of the stock. For example, in the bleaching of sulfate pulp, an operation which was considered impractical and uneconomical until only a few years ago, the procedure might include the following steps, if not more—(1) chlorination, (2) wash, (3) caustic extraction, (4) wash, (5) hypochlorite oxidation, (6) wash.

The equipment now in use for carrying out the bleaching operation varies considerably. When the pulp is treated only with calcium hypochlorite, the equipment may consist essentially of one or more tanks, vertically or horizontally positioned, each with some means for agitating the pulp mass; or a rotary spherical pressure vessel may be used, in which case, the rotation of the vessel serves as the means of agitating the stock. Of necessity, if only a single tank is used, bleaching is carried out as a batch operation, whereas the use of a series of tanks permits either batch or continuous operation. Whatever the nature of the hypochlorite bleach installation, the bleached pulp must be washed with water to free it of traces of bleach liquor as well as to remove the soluble impurities.

There are numerous possible variations in multi-stage bleaching procedure. Practice depends primarily upon the species of wood pulped, the nature of the pulping operations, the acceptance of a given system, and the use requirements of the pulp.

Sodium chlorite bleaching of chemical wood pulp is a recent development. In this process of bleaching, the chlorite may be activated by acid, hypochlorite or chlorine. The use of chlorine and hypochlorite in the earlier stages of the bleaching operation, followed by the chlorite treatment in the final stage, has proved most satisfactory.

In the bleaching of any pulp, the four most important operating factors are time, temperature, stock consistency, and pH. These factors are intimately related, and it is the balancing of them that largely determines the economy of the bleaching operation and the quality of the resulting pulp.

After the washing operation, the bleached pulp may be further dewatered or thickened, particularly if it is to be stored or shipped, or it may be left in slush form for immediate conversion into paper.

Processing other Fibrous Materials. When it is desired to de-ink waste paper, it is common practice to use a soda ash liquor for the cooking operation. Other chemicals, used alone or in various combinations, that have been employed for this operation are caustic soda, lime, borax, soap, silicate of soda, turkey red oil, and fuel oil. Such chemically-cooked waste paper is washed carefully and then bleached much in the same manner as virgin chemical pulp.

Not all rags are boiled or cooked, but in operations where this practice is followed, particularly in mills making high-grade papers, lime, caustic soda, or a mixture of soda ash and lime are the commonly used cooking chemicals. Based on the weight of the rags, the quantity of chemicals in a rag cook may range from 1 to 10 per cent for caustic soda and from 5 to 20 per cent for lime. Cooking pressures range from 15 to 50 pounds; and the cooking time, from 2 to 15 hours.

The purpose of rag cooking is to loosen dirt and to saponify or dissolve grease so that these materials can be removed by washing, and also to act upon colors to facilitate later bleaching. The washing operation is carried out in a machine resembling a Hollander beater (see Conditioning the Furnish) but, in addition, it is equipped with one or more washing devices. This machine is also used to reduce the cooked rags to a fibrous mass, known as half stuff, which, after bleaching with a calcium hypochlorite liquor, is ready for conversion into paper. Old rope is handled in very much the same way as rags.

Cotton linters usually are purified by cooking in caustic soda solution for several hours under a pressure of 80 to 100 pounds. The quantity of caustic soda employed in such a cook approximates 15 per cent of the weight of the raw linters. The cooked fiber, after washing and bleaching, may be dried and baled for shipment or storage, or it may be used in slush form.

A milk-of-lime liquor or a liquor made by combining milk-of-lime and soda ash is usually employed for cooking straw. The amount of lime required for a milk-of-lime liquor approximates 10 per cent of the weight of the straw; whereas the cooking procedure calls for a steam pressure of 35 to 45 pounds for 8 or 10 hours. After the cooking operation is completed, the straw, dumped from the cooker, is allowed to ripen or season in a drainer room or pit for a period of several days. It then is washed and broken down in much the same way as cooked rags, the essential difference in the two operations being that rags are reduced only to half-stuff while the straw fiber receives its full beating treatment (see Conditioning the Furnish).

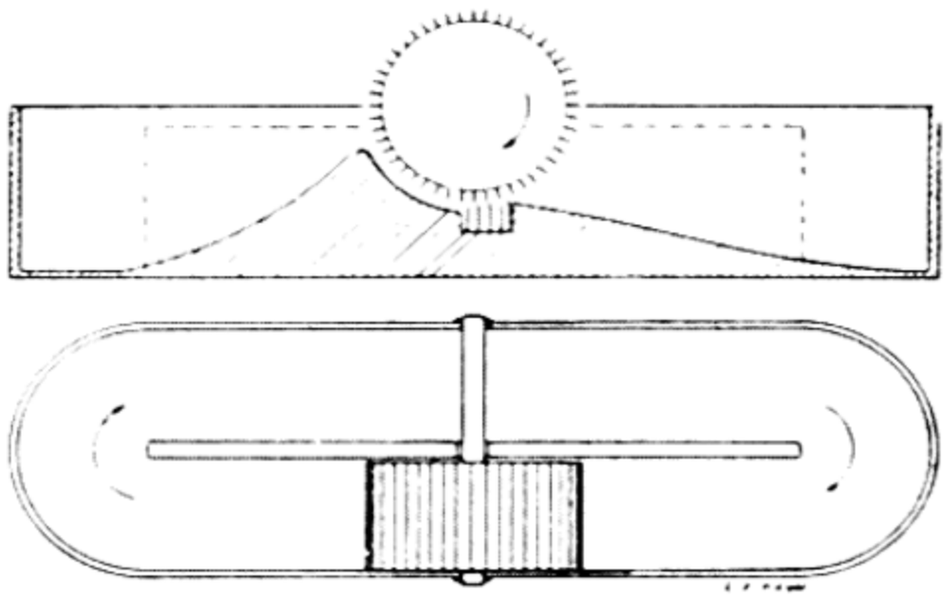


FIGURE 167.—The Hollander beater; upper drawing, a vertical cross-section through the roll side; lower drawing, a top view.

Conditioning the Furnish. Broadly speaking, the processes involved in making a sheet of paper can be divided into two phases: namely, conditioning the furnish, and sheet fabrication. The term "furnish" is used collectively to represent the fibrous and non-fibrous materials that are blended together in water suspension to ultimately produce a paper of certain desired characteristics; sheet fabrication refers simply to the production of the paper on a papermaking machine.

The nature of the furnish and the method of conditioning it vary with the kind and grade of paper, and even with individual mill practice. To cite a few cases in point: Book paper is a general term applying to a group of papers, exclusive of newsprint, which are formulated and produced in such a way as to make them suitable for use in the graphic arts. Chemical

wood pulps, mechanical pulp, selected waste paper, and rag pulp commonly make up the fibrous constituents of such paper. Ordinarily, book paper is made of a mixture of two or three of these pulps, such as a mixture of sulfite and soda; sulfite, soda, and waste paper; sulfite and groundwood; etc.

"Board" is also a very general term. It is used to designate certain papers which range from 0.006 to 0.012 inch or more in thickness. Chemical wood pulps (particularly sulfate and sulfite), semi-chemical pulp, mechanical pulp, waste paper and straw fiber serve as the fibrous raw materials for

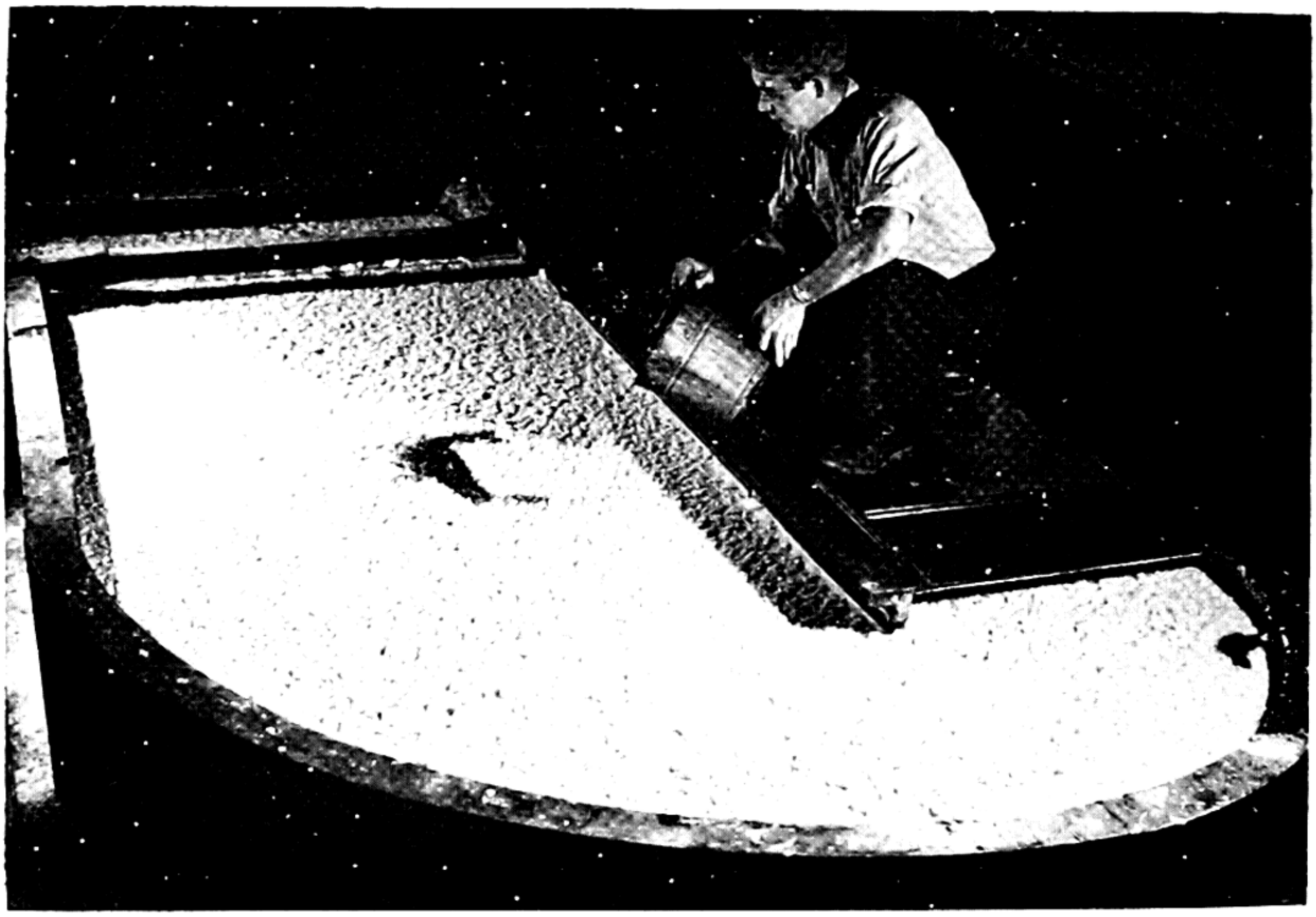


FIGURE 168.—A view of the beater in a paper mill. (Courtesy of the Riegel Paper Corporation, New York, N. Y.)

most boards. Some boards are made from only one kind of fiber, such as sulfate fiber for kraft board or straw fiber (wheat, rye, or oat) for straw-board; others, from mixtures of at least two fibrous materials, such as sulfite and groundwood for bottle cap board, waste paper and some chemical pulp for boxboard; and still others, from various fiber mixtures for each of several plies of the sheet, such as kraft pulp, waste kraft paper, and old newspapers for the outer plies, and chemical pulp screenings (rejects), sulfate pulp, and mixed papers for the center, in container board.

Newsprint, as previously indicated, commonly is made from a mixture of mechanical pulp and sulfite pulp, about 75 to 80 per cent of mechanical pulp and the remainder of unbleached sulfite pulp. One notable exception to this practice is the use of bleached sulfate pulp by one newsprint mill in the South for the chemical pulp portion of its newsprint paper.

The term "wrapping paper" applies to a broad classification of papers in which strength and pliability are essential characteristics. Here again is the possibility of a large variety of furnishes. Sulfate pulp, sulfite pulp, groundwood pulp, straw, waste papers, rope and other fibrous materials find use in its production.

Writing paper denotes paper suitable for use with typewriter, pen and ink, or pencil, or for printing. The fiber furnish commonly determines sheet quality. It ranges from 100 per cent rag, mixtures of rag and chemical pulp, 100 per cent chemical pulp, to mixtures of chemical and mechanical pulps.

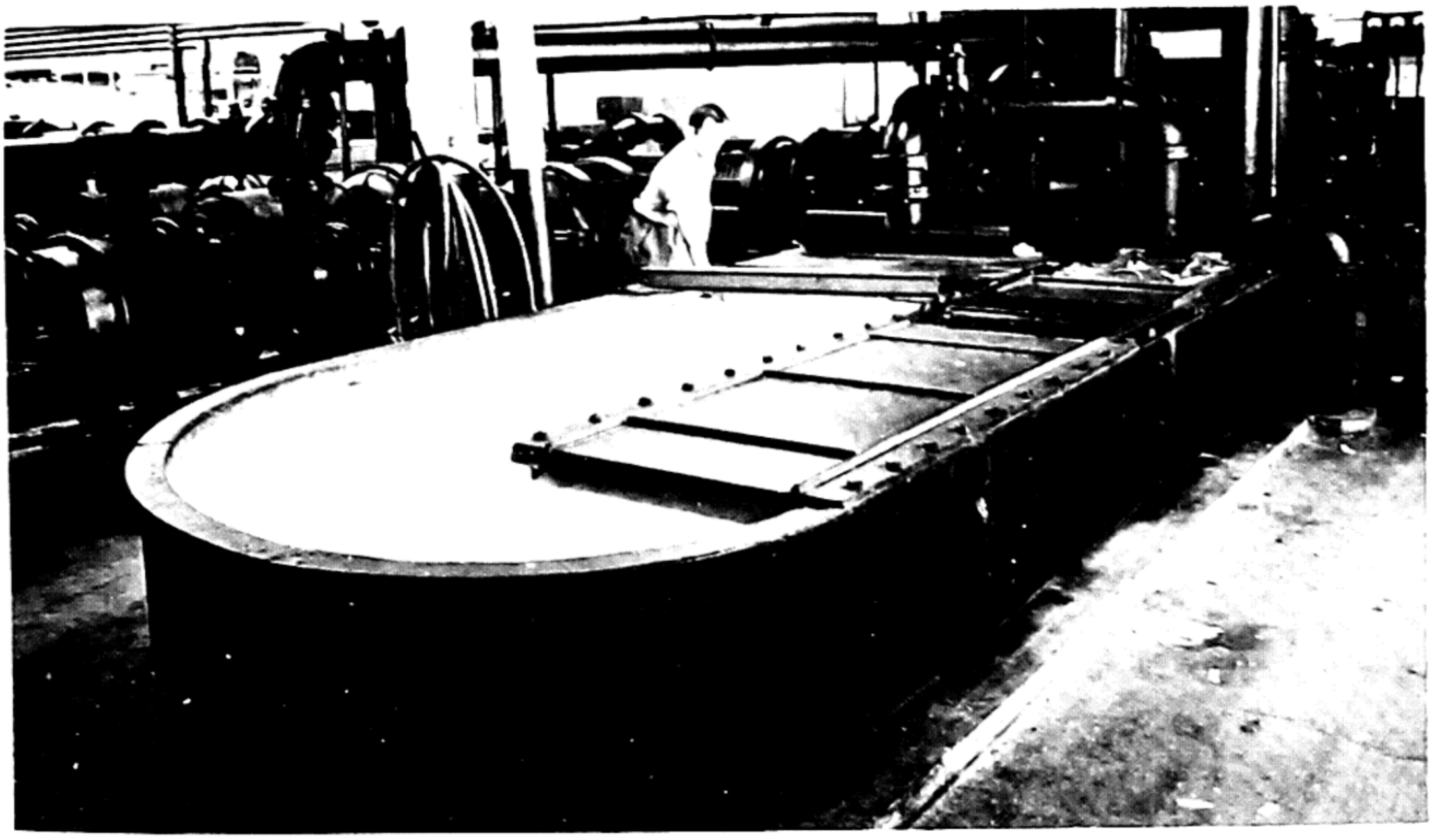


FIGURE 169.—A Tugboat beater in a paper mill. The beater and pulping element are on the lower level. (Courtesy of the Riegel Paper Corporation, New York, N. Y.)

The kind of paper being made determines the need for non-fibrous raw materials in the furnish as well as the material or materials to use. A few of the more common materials used for this purpose are rosin size, alum, dyestuffs, sodium silicate, starch, clay, titanium pigments, talc, blanc fixe, precipitated calcium carbonate, zinc sulfide, and urea-formaldehyde and melamine resins. (Addition of melamine resin to the furnish commonly is delayed until just before it is fabricated into a sheet.) Each of these materials, as well as numerous others, are used to impart very definite characteristics to finished papers.

The equipment used for blending the various components of the furnish as well as for hydrating and altering the surface character of the fibers has witnessed numerous changes in design within recent years. In brief, this stock conditioning equipment may be classified generally into the following types—Hollander beater, jordan, disc, hydraulic, and rod mill.

The Hollander beater has been used in papermaking for many years. It is characterized by an oval-shaped tub with an impartial partition extending lengthwise through its center, a hooded, horizontally positioned roll with laterally placed bars on its face, and a bed-plate arrangement so located in the bottom of the tub to permit bar-to-bar action between it and the

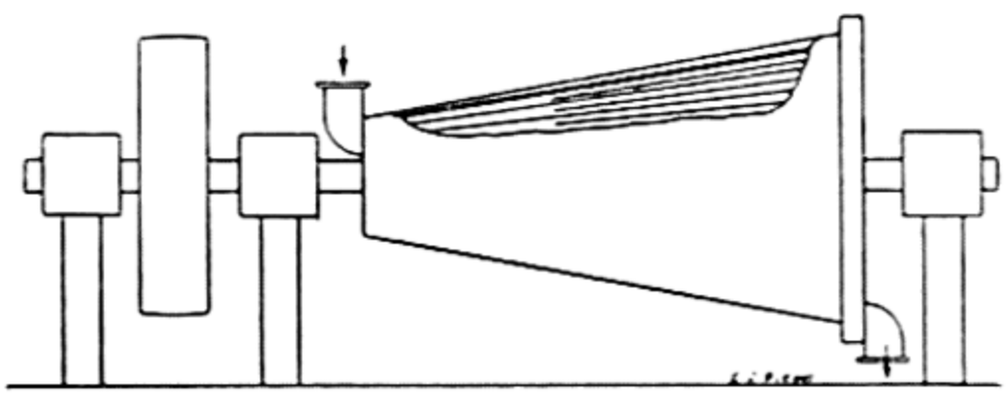


FIGURE 170.—The jordan or conical refiner.

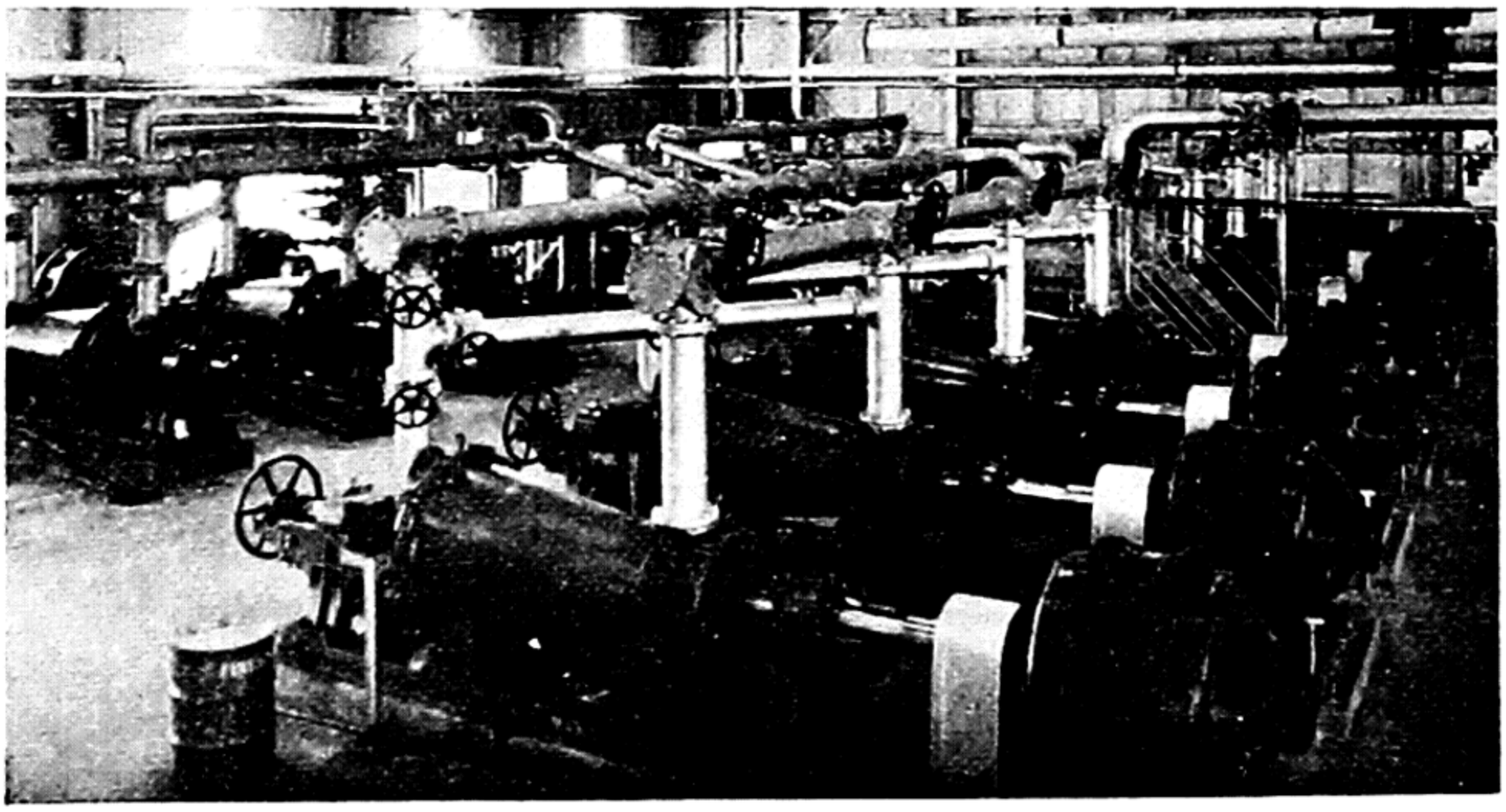


FIGURE 171.—A double row of jordans in a large paper mill. (Courtesy of *Paper Industry and Paper World.*)

roll. In fact, so important has been the functioning of the machine, that the aphorism, "Paper is made in the beater," has long been associated with the industry.

A beater which is also a pulper is the Miami Tugboat Pulper, a modern successor of the Hollander. (See Fig. 170.) The midfeather type tub has a sloping bottom, leading to the pulping chamber at a lower level; the rotating element has a tip speed about three times as high as the impact velocity of a beater roll. The stock is returned to the tub, and is circulated. The Tugboat Beater is a high-capacity device.

The jordan consists essentially of a horizontally positioned conical shell within which rotates a correlative cone-shaped plug. Both the inside of the shell and the outer surface of the plug are fitted with bars; and, through adjustment of the plug, the desired bar clearance between the shell and plug is established.

Designs of disc-type machines in use include both single disc and double disc units with the respective disc or discs rotating in a vertical plane.

In the hydraulic system, stock is impinged from a jet at high velocity

against a target of special design or against an oppositely directed jet of stock; in the rod mill, stock is acted upon by the crushing action of a comparatively heavy weight of metal rods which roll over one another within a revolving, horizontally positioned, cylindrical shell.

There also are a number of other designs of stock-conditioning equipment; but in each case, like that of the equipment already mentioned, it has for its purpose the conditioning of the furnish to an end-point which will give desired results when fabricated into paper. To supplement the work of this equipment and to permit final control of the stock before fabrication is a jordan installation. If jordans are being used for the initial or

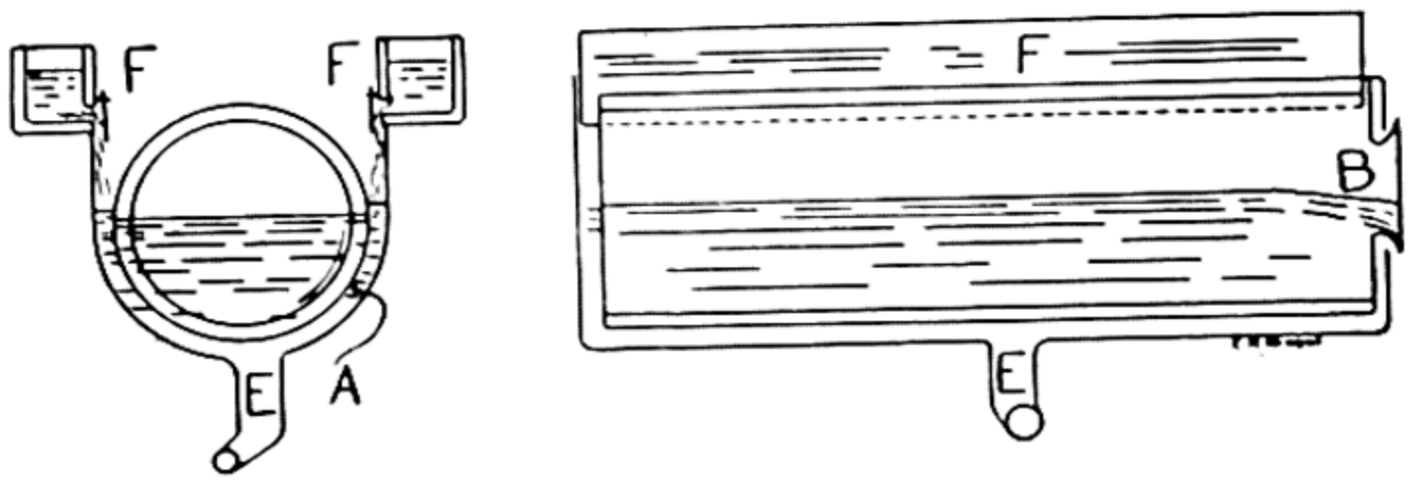


FIGURE 172.—Inward flow screen for paper stock. *A*, slotted screen which rotates; *B*, open discharge for cleaned stock; the vat itself is shaking in horizontal plane; *E*, waste pipe for tailing removal; *F*, flow boxes. Driving and shaking mechanism not shown.

primary stock treatment, as is the case in a number of mills, particularly in the South, they may be grouped with the finishing jordans in a single convenient arrangement.

After the stock has passed through the finishing jordans, usually at a density of about three per cent, it is diluted to a consistency of approximately one per cent. At this consistency it is ready for screening and possibly other purification, after which it is delivered to the paper machine. The purpose of this screening operation is two-fold—first, to remove as much dirt or undesirable solids from the stock as possible; secondly, to obtain a better separation of fibers so that, when the stock is delivered to the paper machine, better felting of the fibers will result. In most mills, this screening of the stock completes the conditioning of the furnish; but further dirt removal is accomplished by some mills in a supplementary operation where a more dirt-free sheet is desired.

The screening of the stock is accomplished in machines designated as paper machine screens as contrasted with the pulp screens of the pulp mill. These screens commonly are of two types—either diaphragm or flat (similar to the screen of the same designation used for screening pulp), or rotary.

There are two types of rotary screen—the inward flow and the outward flow. In the inward flow screen, accepted stock passes inwardly from a vat through slots of a screen-plate cylinder positioned within it. The cylinder is open at one end, and this end serves as the discharge for the accepted stock. Rejects, in turn, are removed from the bottom of the vat. Conversely, in the outward flow screen, stock to be screened enters the screen-

plate cylinder. The accepted stock passes through the openings in its plates into a vat beneath it; the rejects, in turn, are removed from within the cylinder by the use of a discharge pan located within it.

Dirt too small in size to be rejected in screening may be separated from the screened stock, if necessary, by equipment which, for its functioning, depends upon the difference in specific gravity of the dirt and the fiber.

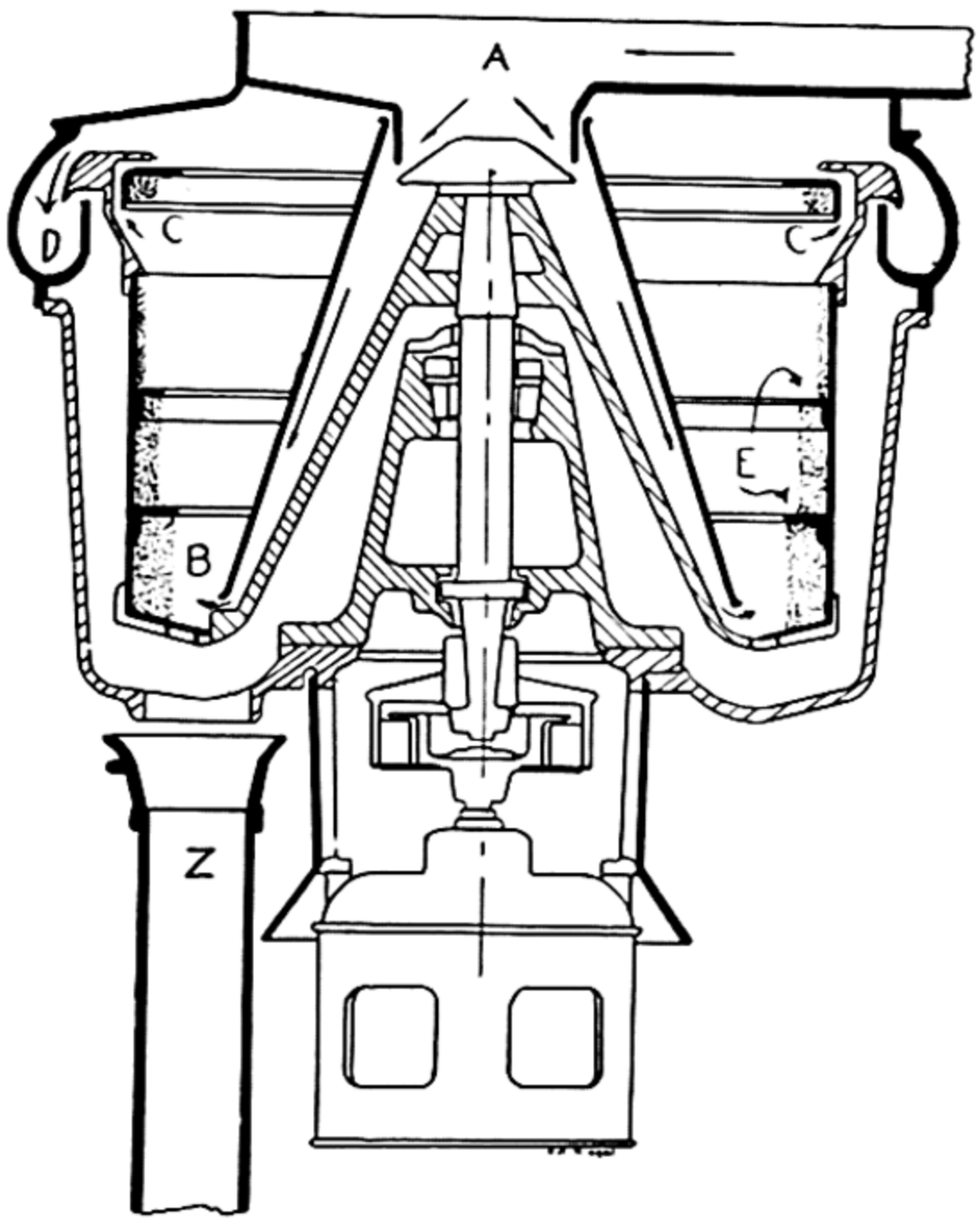


FIGURE 173.—Centrifugal device for removing dirt from paper stock. *A*, raw stock inlet; *B*, matte with dirt retained by angular baffles *E*; light dirt caught by annular skimmer *C*; *D*, cleaned stock, with outlet to paper making machine; *Z*, waste pipe for washings.

Such equipment may employ centrifugal force to effect the separation; or separation may be accomplished by increasing considerably the weight differential between the dirt and the stock by use of a pressure differential device.

Fabrication of the Sheet. The making of a sheet of paper on a paper machine involves dewatering of the stock and the surface finishing of the sheet. The dewatering of the stock must be accomplished in a manner that produces a sheet of uniform structure and thickness. It is done through the application, in combination, of natural drainage, induced drainage by partial vacuum, roll pressure, and heat; while surface finishing of the sheet, in general, is accomplished by rolling friction. These operations are performed by either one of two types of paper machine—a fourdrinier machine or a cylinder machine.

The fourdrinier machine is characterized by the use of a traveling wire cloth, commonly designated as the wire, for the felting of the sheet. This wire is supported by tube rolls in such a way that the portion of it receiving the wet stock from a head box immediately preceding is traveling forward in a horizontal or nearly horizontal plane. In addition to traveling forward, the wire usually is given a sidewise motion or shake. This movement effects better intertwining of the fibers upon the surface of the wire as the water in which they are suspended drains through it. Removal of water

from the forming sheet is hastened by the addition of suction boxes to the underside of the sheet-carrying portion of the wire. Considerable water not removed by natural drainage is evacuated through these boxes by applying partial vacuum to their drainage area.

By the time the sheet reaches the forward end of the wire, sufficient water has been removed from it so that it can support its own weight. At this point it is conveyed by means of woolen felts or blankets through a series of roll-type presses. Not only do the presses remove additional water from the wet sheet but they also compact it. The compacted sheet then passes to the drier section of the machine where approximately two pounds of

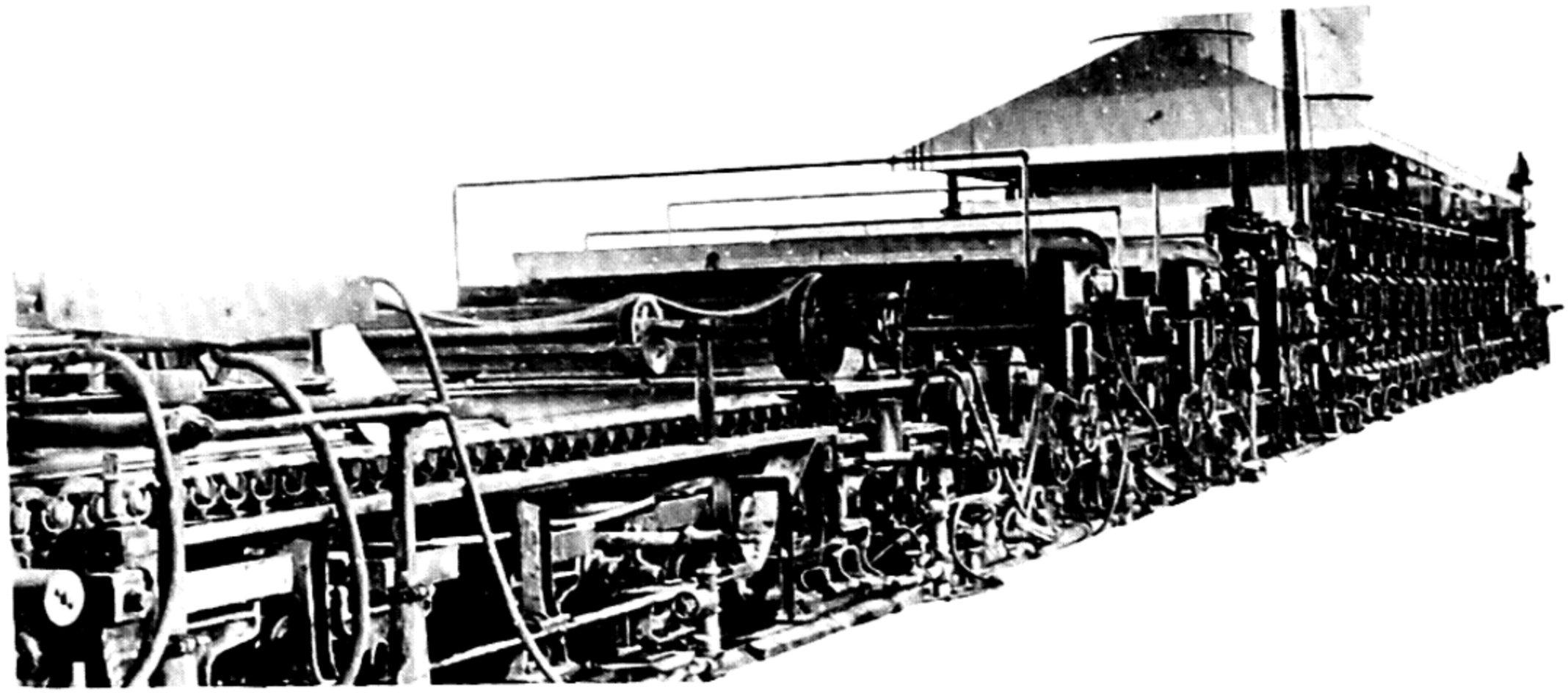


FIGURE 174.—Fourdrinier paper machine with sheet-forming section in immediate foreground. (Courtesy of Beloit Iron Works.)

water are removed from it for each pound of paper produced. This section commonly is made up of a series of steam-heated cast-iron cylinders, the number and size of which depend upon the grade of paper being produced and upon the speed at which the machine is operated.

After the drying of the sheet, it is necessary to improve its surface. This finishing operation is accomplished by passing the sheet through a vertical stack of horizontally positioned, highly polished, chilled cast-iron rolls, known as the calender or calender stack. In this arrangement, power is applied to the bottom roll, the other rolls revolving simply through frictional contact.

As the sheet leaves the calender it is wound into a large roll by means of a reel. The reel is designed to permit continuous operation of the machine. When a roll reaches a suitable diameter, the sheet is broken and another roll started. The first roll is then slit and rewound into rolls of paper of the proper width for marketing or for immediate conversion into a wide variety of paper products.

The sizes of fourdrinier machines, commonly designated by width of wire, vary widely. The widest fourdrinier in North America has a wire width of 304 inches. As originally installed, this machine had a length

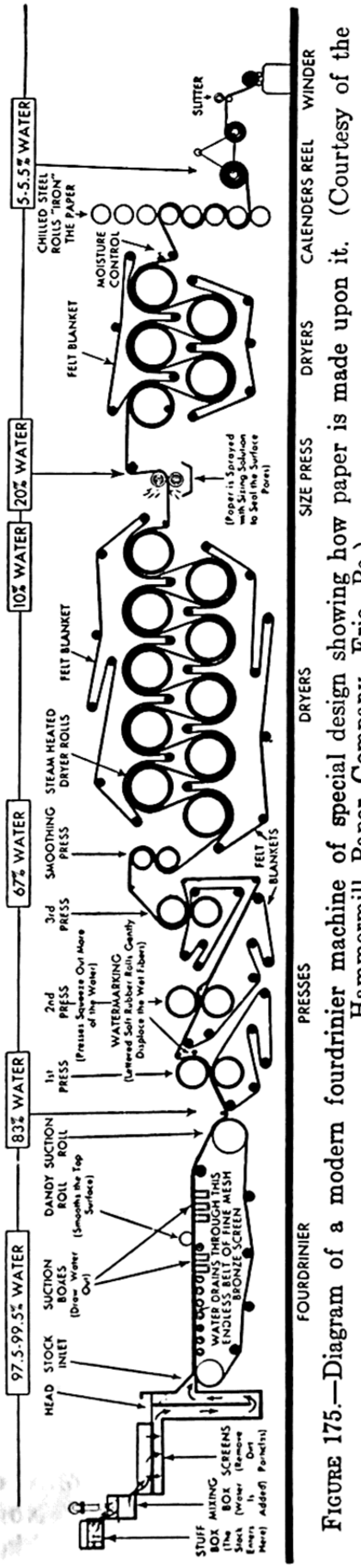


FIGURE 175.—Diagram of a modern fourdrinier machine of special design showing how paper is made upon it. (Courtesy of the Hammermill Paper Company, Erie, Pa.)

of 296 feet. It weighed approximately 2100 tons, the rolls in the calender stack alone, an eight-roll stack, weighing 150 tons. Likewise, the drier section included 48 drying cylinders, each with a diameter of 60 inches and a face length of 302 inches. These driers weighed 13 tons apiece.

Operating on newsprint, the daily productive capacity of this machine considerably exceeds 200 tons.

The cylinder paper machine, differing from the fourdrinier machine principally in the manner of felting the sheet, receives the paper stock in one or more vats. Partially submerged in each vat is a cylinder mold with a surface of wire cloth. As the mold revolves, the sheet is felted to the wire

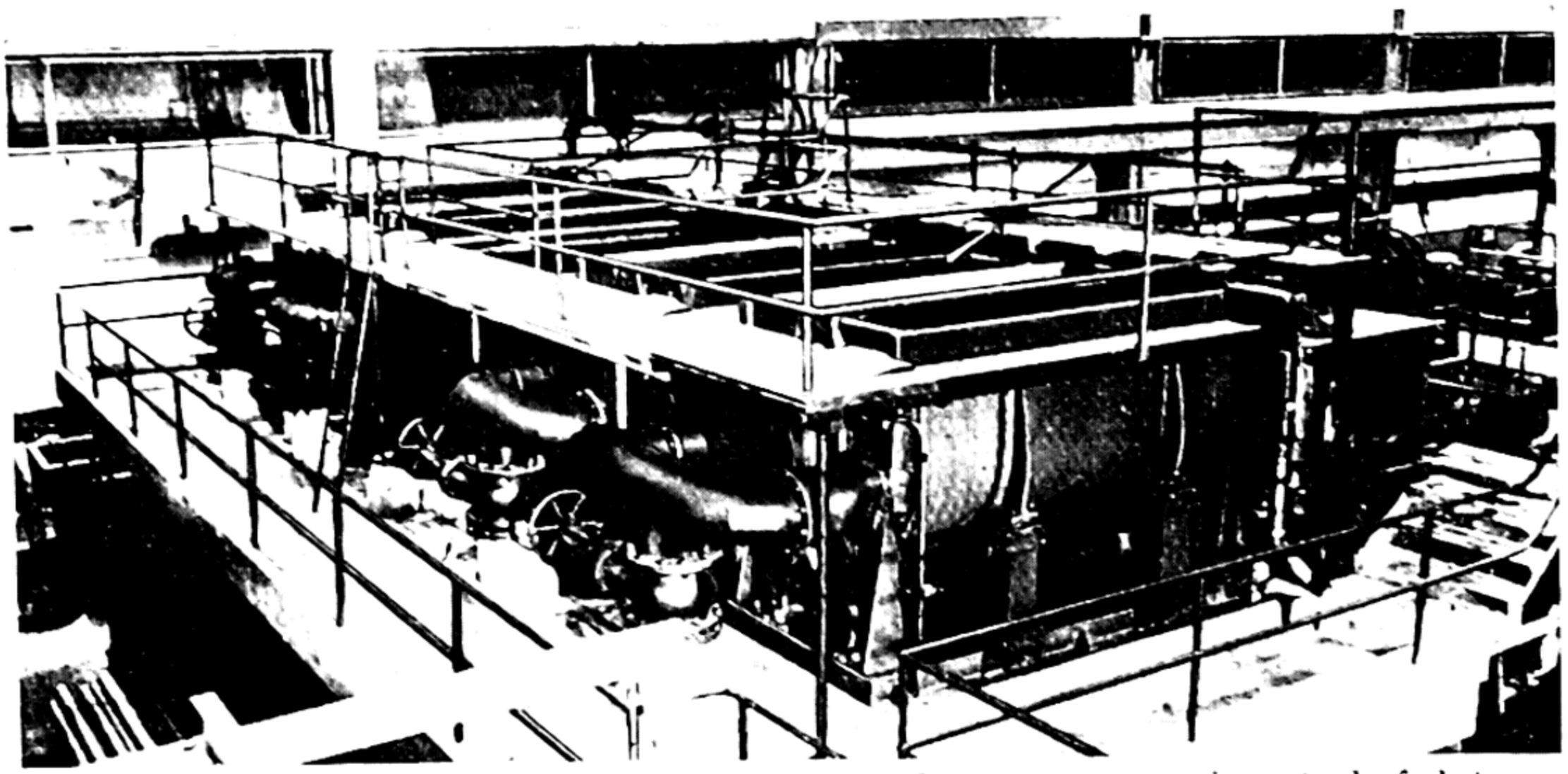


FIGURE 176.—Installation comprising four inward flow screens serving stock fed to a 262 inch newsprint paper machine. (Courtesy of the Bird Machine Company, East Walpole, Massachusetts.)

cloth by the drainage of water to the interior and from which it is discharged. The wet sheet thus formed is removed from the unsubmerged portion of the cylinder by means of an endless woolen felt or blanket, which also carries it through a series of squeeze rolls and a roll-type press similar to that of a fourdrinier machine. The squeeze rolls and the press compact the sheet and remove considerable water from it. More water is removed and the sheet is further compacted by passing the sheet through two or possibly three additional presses. After the pressing operation, the sheet passes over steam-heated drying cylinders, through a calender stack arrangement, and to a reel just as in the case of the fourdrinier machine.

When more than one vat is used in combination, five or six cylinder machines being rather common and even more cylinders being used in some instances, a sheet of several plies, one ply for each mold, is built up on the single felt which contacts the unsubmerged area of each cylinder. This multi-layer sheet, like the sheet from a single cylinder machine, is subjected to mechanical pressure both to compact the fiber mass and to remove water from it. Then, too, the pressing operation brings the several layers so

closely together that, after drying, they form to all intents and purposes an integrated sheet.

There are several modifications of the fourdrinier and cylinder types of paper machines. Probably the two most important of these modifications would be the Harper fourdrinier and the Yankee machine. In the Harper fourdrinier machine, the wire runs away from the presses rather than toward them, the first or wet end section of the machine being in reverse to the usual fourdrinier. The sheet formed on the wire is removed from it by a

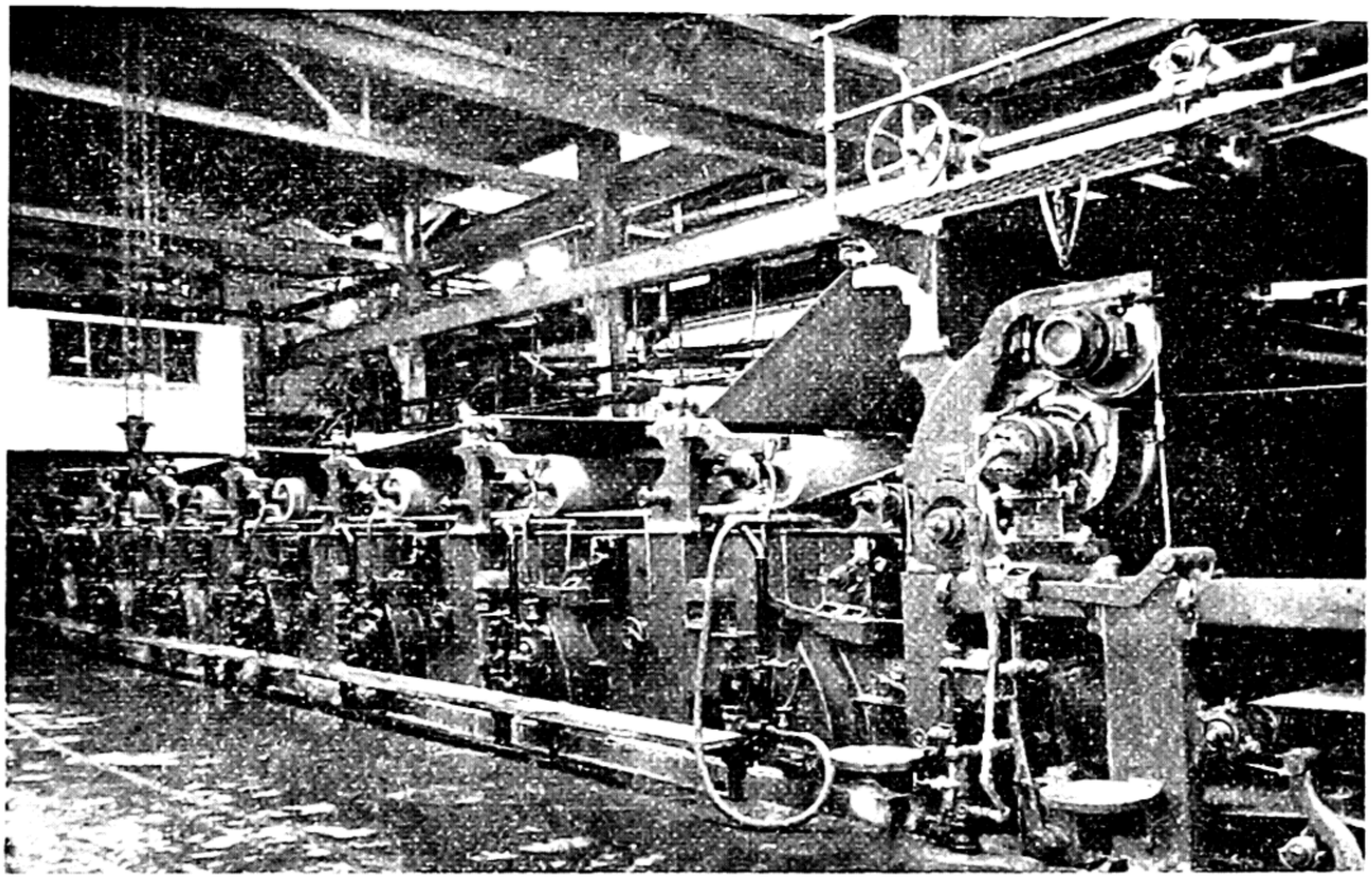


FIGURE 177.—Wet end or forming section of multi-cylinder papermaking machine. (Courtesy of Black-Clawson Co.)

long felt which, extending over the forming section, delivers it to the press section of the machine. This feature of the machine makes it especially satisfactory in the manufacturing of lightweight papers.

The Yankee machine is characterized by its drier arrangement. It commonly features a single, highly-polished, large diameter drier, with or without auxiliary driers. The range in diameter for a Yankee drier usually is from 9 to 15 feet. Such a drier imparts a glossy finish to one side of the

TABLE 70.—*U. S. paper and paperboard production by kinds (1946).*

	Quantity in short tons		Quantity in short tons
Newsprint	772,797	Sanitary paper	860,658
Groundwood paper	775,779	Tissue paper	183,837
Book paper	1,933,428	Absorbent paper	102,811
Fine paper	1,160,411	Building paper	1,021,578
Coarse wrapping converting and bag paper	2,690,490	Paperboard	8,528,582
Special industrial paper	271,643	Building Board	975,653
		U. S. Total	19,277,667

paper, and is particularly adapted to the manufacture of thin and medium weight papers such as are used in the lining of duplex paper bags, toilet tissue, etc.

Industrial chemistry has played an important part in the development of the modern pulp and paper industry. The very nature of its processing operations, which have been only briefly outlined, has demanded it. Likewise, in all probability, its role will become of constantly increasing importance.

TABLE 71.—*U. S. paper and paperboard production by states (1946).*

State	Quantity in short tons	State	Quantity in short tons
New York	1,738,513	Georgia	353,885
Michigan	1,469,637	Alabama	341,526
Ohio	1,370,762	Oregon	337,018
Wisconsin	1,330,054	North Carolina	281,110
Pennsylvania	1,233,488	New Hampshire	216,115
Maine	1,194,918	Tennessee	190,965
Louisiana	1,190,060	Vermont	98,707
New Jersey	970,974	Delaware	47,058
Washington	735,080	West Virginia	22,980
Virginia	703,974	Arkansas and Texas	371,677
Illinois	693,401	Rhode Island and Connecticut	334,436
Massachusetts	691,337	Maryland and District of Columbia	250,868
South Carolina	562,847	Iowa, Missouri, Kansas and Colorado	198,181
Minnesota	560,010	U. S. Total	19,277,667
Florida	550,786	U. S. Total (1947)	21,114,000
Mississippi	456,606		
California	419,402		
Indiana	361,292		

OTHER PATENTS

U. S. Patent 1,837,309, production of sulfite pulp and recovery of the acid employed; 1,872,996, process of making pulp, subjecting the treated material to a steam pressure of over 250 pounds/sq. in. and discharging at that pressure so that the material is exploded and thoroughly disintegrated; 2,031,974, recovery of chemicals from waste pulping; 2,069,185, manufacture of vanillin from waste sulfite pulp liquor.

PROBLEMS

1. A soda pulp digester has a capacity of 820 cubic feet. It contains at the end of the cook 220 cubic feet of cellulose fibers. In the remaining space, a volume equivalent to 500 cubic feet of cold 5 per cent caustic soda, with specific gravity of 1.05, is introduced. What was the weight of the cold caustic liquor, how much caustic soda in pounds did it contain, and what was the volume of the 5 per cent caustic soda solution in gallons?

2. A sulfite pulp digester has a capacity of 3000 cubic feet; it contains a 6 per cent calcium bisulfite solution to the extent of two-thirds of its volume, measured cold. Let the specific gravity of the solution be 1.07. How much calcium bisulfite is represented, how much sulfur dioxide, and how many pounds of sulfur would be required for the production of one-half this quantity of sulfur dioxide?

3. A wood contains 50 per cent cellulose. It is desired to produce 56 tons of a certain paper per day, from chemical pulp. How many cords of wood will be required, using the values given in the text? The yield of paper on the basis of cellulose in the wood is 90 per cent.

Reading References

"Paper making and its machinery," T. W. Chalmers, London, Arnold Constable, Ltd., 1920.

"How the United States can meet its present and future pulp-wood requirements," Earle H. Clapp and Charles W. Boyce, *U. S. Dept. Agr. Bull.* No. 1241, July, 1924.

"Purified wood fiber," Geo. A. Richter, *Ind. Eng. Chem.*, 23, 266 (1931).

"The Masonite process for Presdwood," R. M. Boehm, *Ind. Eng. Chem.*, 22, 493 (1930).

"Cellulose in Virginia, I—Pulp and paper," L. B. Hitchcock, *Ind. Eng. Chem.*, 22, 488 (1930).

"The Celotex and cane sugar industry," E. C. Lathrop, *Ind. Eng. Chem.*, 22, 449 (1930).

"Papermaking through eighteen centuries," Dard Hunter, New York, William Edwin Rudge, 1930.

"Georgia pines for sulphite pulp and newsprint," S. L. Handfoth and J. N. Tilley, *Ind. Eng. Chem.*, 26, 1287 (1934).

"The development of paper manufacture from southern pines," R. H. Stevens, *Trans. Am. Inst. Chem. Eng.*, 25, 201 (1930).

"Some aspects of the manufacture of fibrous cellulose," J. L. A. MacDonald, *J. Soc. Chem. Ind.*, 46, 251T (1927), with emphasis on esparto pulp manufacture.

"Paper making undergoes many changes," Clark C. Heritage, *Chem. Met. Eng.*, 44, 9 (1937).

"Tomorrow's stock preparation—today," Joe Baxter, *Paper Mill and Wood Pulp News*, June 17 and 24, 1939.

"Trends in wood pulp industry," Harold R. Murdock, *Chem. Met. Eng.*, 44, 4 (1937).

"Nitration of purified wood fiber," M. O. Schur and B. G. Hoos, *Ind. Eng. Chem.*, 29, 26 (1937).

"Manufacture of pulp and paper," 3rd ed., by the Joint Textbook Committee of the paper industry of the United States and Canada, in 5 volumes, of which 3, 4 and 5 were published in 1938, New York, McGraw-Hill Book Company, 1938.

"The background and economics of American paper making," Louis Tillotson Stevenson, New York, Harper and Brothers, 1940.

"Chemistry of pulp and paper making," 3rd ed., Edwin Sutermeister, New York, John Wiley and Sons, 1941.

"The newsprint paper industry," John A. Guthrie, Cambridge, Harvard University Press, 1941.

"Modern pulp and paper making," 2nd ed., G. S. Witham, Sr., New York, Reinhold Publishing Corp., 1942.

"Cellulose, its history, growth, and influence," Merle Heath, *Chemical Industries*, 62, 405 (1948).

"Problems in materials separation on a Fourdrinier paper machine," C. A. Sankey and B. Cowan, *Chem. Eng. Progress*, 44, 745 (1948).

The chief natural fibers used for articles of clothing are cotton, linen, wool and silk; to these have been added through the chemist's ingenuity a number of synthetic fibers, among which are rayon, acetate rayon, Vinyon, and nylon.

Chapter 22

Synthetic Textile Fibers*

Rayon

Today the most important synthetic textile fiber is rayon. Chemically conceived as early as 1664 but not produced commercially in France until 1890, rayon has risen rapidly to a position of prominence in the textile world. This prominence is indicated by the fact that in 1940 rayon was produced in greater quantities throughout the world than was wool.

Rayon may be defined as a man-made textile yarn or fiber whose chemical base is cellulose. More exactly defined, "Rayon is the generic term for filaments made from various solutions of modified cellulose by pressing or drawing the cellulose solution through an orifice and solidifying it in the form of a filament." This definition covers those fibers composed of a chemical compound of cellulose (*e.g.*, cellulose acetate) as well as those formed by the regeneration of cellulose from a chemical solution (*e.g.*, viscose, cuprammonium, or nitrocellulose).

The term "rayon" was coined in the United States in 1924 for the purpose of replacing the term "artificial silk" as a name for these cellulose-base synthetic fibers. This term is now generally accepted throughout the world as a generic name for this family of textiles.

Two primary products now are made by the industry, namely, continuous filament rayon yarn and rayon staple fiber. By way of differentiation, rayon filament yarn may be described as being made of a number of fine, continuous rayon filaments, grouped and lightly twisted together. On the other hand, rayon staple fiber is made by cutting rayon filaments into uniform lengths which are subsequently spun into yarn in the same manner as cotton or wool. The resulting textile yarn is called "spun rayon yarn." Secondary products made by the rayon industry are rayon strips and narrow tubular forms known as artificial straw, and rayon monofil (artificial horsehair); related products are cellophane, bottle seals and cellulose sponge.

Growth of Rayon Production

The growth of the rayon industry throughout the world in the sixty years of its existence has been unusually rapid. In 1890 the world output of rayon amounted to a mere 30,000 pounds, whereas in 1940 it was 2,380,000,000 pounds. The world production suffered greatly by the dislocation caused by the war. The production in 1940 was as shown in Table 72.

Although the United States in 1940 was the third largest producer in total rayon output, it was by far the world's greatest single producer of rayon fila-

* In collaboration with Dr. Edward F. Wesp, Rayon Department, E. I. du Pont de Nemours and Company, Inc., Buffalo, N. Y.

TABLE 72.—*World production of rayon, by countries.*
(Rayon filament yarn plus rayon staple fiber)
(in millions of pounds)

	1940	%
Germany	825	35
Japan	525	22
United States	471	20
Italy	325	14
Great Britain	150	6
All others	84	3
Total	2380	

ment yarn, accounting for 34 per cent of the world output of this rayon product. In the intervening years, its production of the same product has increased still further. It is chiefly in rayon staple that the production of earlier years in Europe and in Asia is missed.

The uses of rayon are varied and numerous. Its application in apparel-type fabrics is now well known. Great quantities of rayon are used in the manufacture of dresses, underwear, hosiery, linings, elastic goods, and in numerous other items of men's, women's, and children's apparel. Household

TABLE 73.—*World production of rayon, by continents.**
(Rayon filament yarn, rayon staple, and rayon tow)
(in thousands of pounds)

	1941	1946	1947 (est.)
Rayon filament yarn			
Europe	606,905	355,495	
No. America	470,705	699,090	
So. America	24,180	38,385	
Asia	168,450	9,685	
	1,270,240	1,102,655	1,290,000
Rayon staple yarn			
Europe	1,134,760	369,450	
No. America	122,025	177,375	
So. America	1,765	1,685	
Asia	296,605	20,490	
	1,555,155	569,000	710,000
Grand total rayon	2,825,395	1,671,655	2,000,000

* The production figures for 1941 were the best for the world total, and the best for Europe; for Asia, the best figures were for 1938, with total rayon 541,410 thousand pounds. See elaborate table with 34 columns in *Rayon Organon* for June, 1947.

uses of rayon include rugs, carpets, blankets, upholsteries, draperies, tapestries, quilts, bedspreads, table linens, etc. There is also a growing use for rayon in industrial products. Noteworthy here is its use in automobile and airplane tires.

Besides its application in these many civilian products, rayon played an important part in World War II. Millions of pounds of viscose rayon were used in tires for the Army's mechanized equipment, in airplane tires, in self-

Note on Figure 178. The site of the Spruance plant is Ampthill, a plantation dating back to Colonial days, and on which General Cary built a house. The latter had to be removed to make room for the plant; it was taken down brick by brick and re-erected nearby, as the deed directed. A burying ground was left undisturbed and is forever accessible to the members of the Cary family. U. S. Highway No. 1 lies just beyond the fine grove of trees, which hide the plant from view.

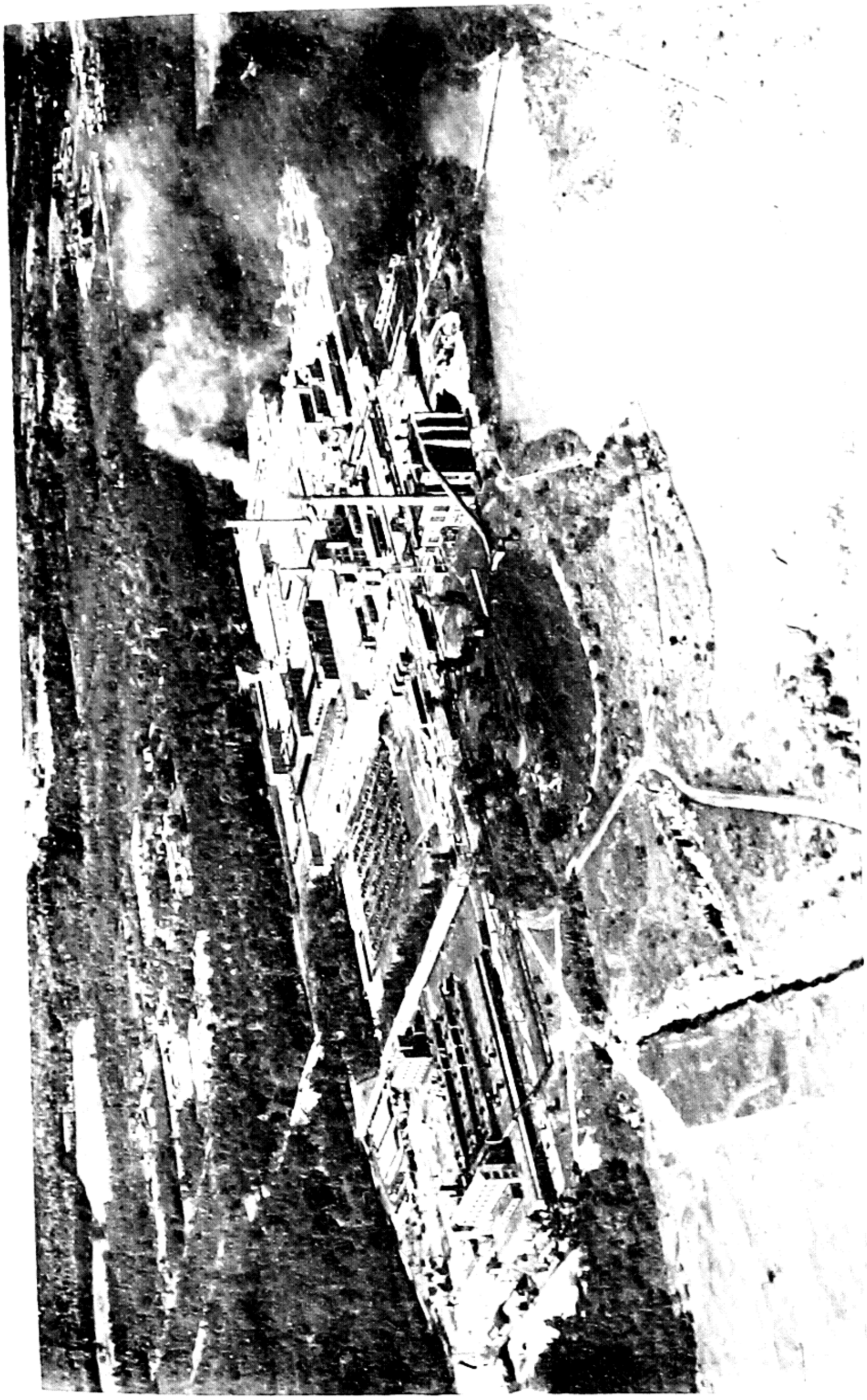


FIGURE 178.—The Spruance rayon plant at Richmond, Virginia, of E. I. du Pont and Company, as seen from the air (by permission).

sealing gasoline tanks for bombers and fighter aircraft, in flare parachute cloth, in cartridge and powder bag cloth, in mine-laying and fragmentation bomb parachute cloth, in paratroop jump suits, wire insulation, helmet linings and assemblies, uniform linings, and many other uses.

The reasons for the increase in the civilian uses of rayon may be attributed to three factors: style, serviceability, and price. Because rayon is a product of chemistry, its production is accomplished under rigid chemical standards of control, whereby its quality and uniformity are assured. At the same time, moreover, its chemical nature makes it possible for rayon producers to develop many innovations in fiber structure and characteristics which in turn are given to consumers in the form of new fabrics. Rayon's behavior with dyes permits almost endless color combinations in fabrics, thus appealing to the fashion habits of the consumer.

The style and serviceability features of rayons are available to the consumer at price levels that are within reach of all income groups. The price of rayon filament yarn and staple fiber have been steadily lowered during the years, the result of improvement in the technique of rayon manufacture and a simultaneous improvement in the quality of the product. For example, the price of 150 denier yarn in 1920 was $6 per pound. The 1948 price for the same denier is about 74 cents per pound.

Methods of Rayon Manufacture in the United States

Rayon filament yarn is produced by three methods in the United States, namely, the viscose process, the cellulose acetate process, and the cuprammonium process. From 1920 to 1934 rayon yarn was also produced here by the nitrocellulose process. This process is the original method of rayon manufacture, invented in 1884, and patented by Count Hilaire de Chardonnet.[1] Yarn by this method was first commercially produced at Bescançon, France, in 1890. Although this process has been discontinued in the United States, it is still used in Brazil and Hungary; however, the output of this type of yarn is very small.

The fundamental principle of rayon yarn manufacturing is the same regardless of the process of manufacture used. A cellulose solution of proper viscosity is prepared and subsequently forced through tiny openings into a medium which coagulates these fine streams as they emerge. By this coagulating action, filaments of cellulose or a cellulose compound are formed which are then conditioned, processed, twisted, packaged as required, and then shipped to textile fabricators.

The size of the filaments so produced is measured in terms of deniers. The denier[2] of a yarn may be defined as the weight in grams of 9000 meters of the yarn. Thus a yarn is said to be 150 denier, if 9000 meters of it weigh 150 grams. Therefore, the lower the denier the finer the yarn; conversely, the higher the denier the coarser the yarn.

The Viscose Process. The viscose process is at the present time the most widely used. United States production of viscose yarn in 1941 accounted

[1] It is pleasant to know that Chardonnet was at one time a student of Pasteur. Chardonnet's basic patent was French Patent 165,349 (1884). [Quoted from Mr. Avram's book "The rayon industry," New York, D. Van Nostrand Co., 1927].

[2] The smallest piece of medieval French money was called a denier.

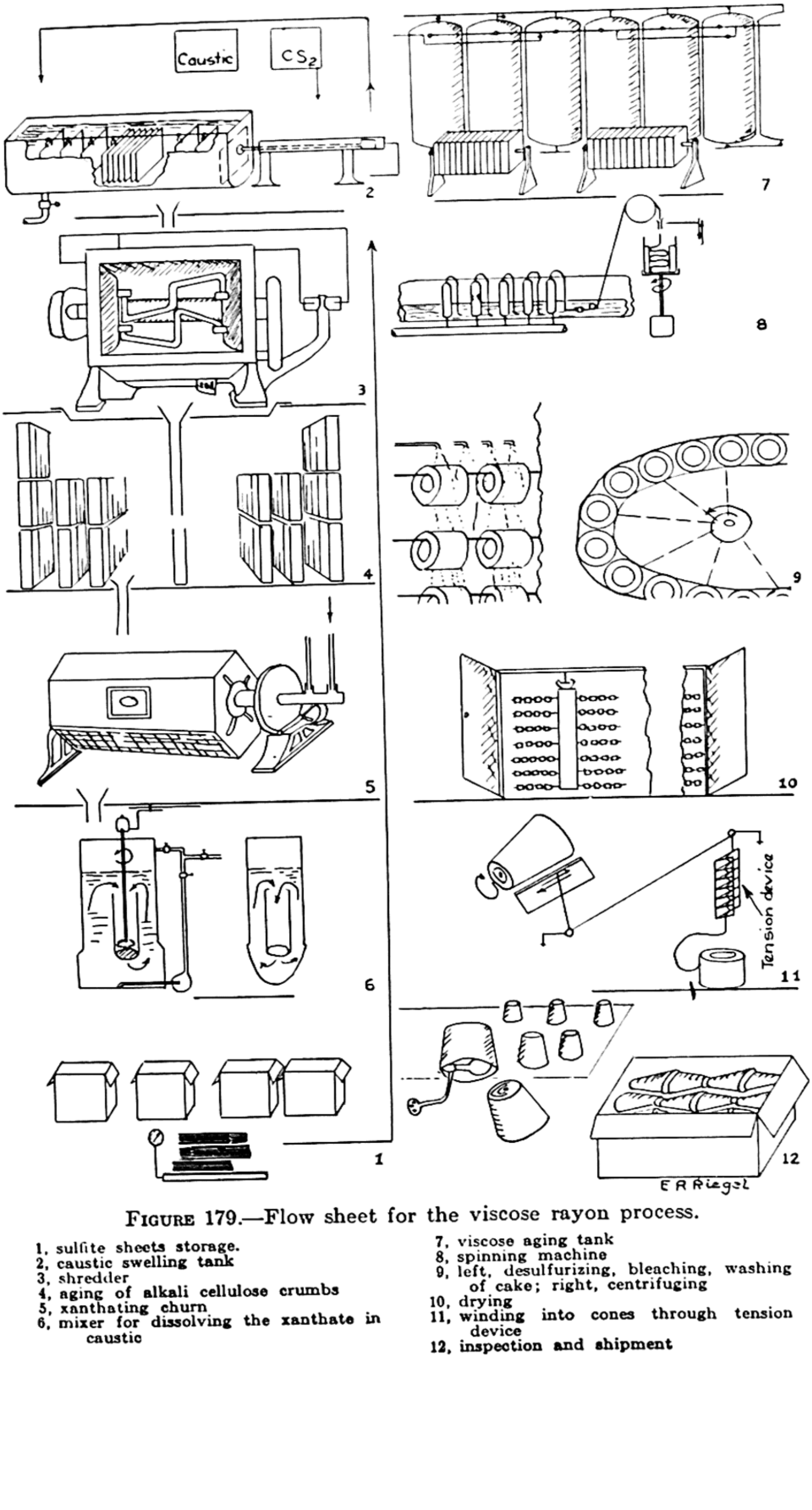


FIGURE 179.—Flow sheet for the viscose rayon process.

1, sulfite sheets storage.
2, caustic swelling tank
3, shredder
4, aging of alkali cellulose crumbs
5, xanthating churn
6, mixer for dissolving the xanthate in caustic
7, viscose aging tank
8, spinning machine
9, left, desulfurizing, bleaching, washing of cake; right, centrifuging
10, drying
11, winding into cones through tension device
12, inspection and shipment

for about 60 per cent of the nation's total yarn output; the proportion of world production is somewhat higher. The principal raw materials used by this process are dissolving wood pulp,[3] refined cotton linters, carbon disulfide, sulfuric acid, caustic soda, glucose, ammonia, magnesium sulfate, sodium carbonate, sodium aluminum sulfate, sodium sulfide, zinc sulfate, and other chemicals in smaller quantities.

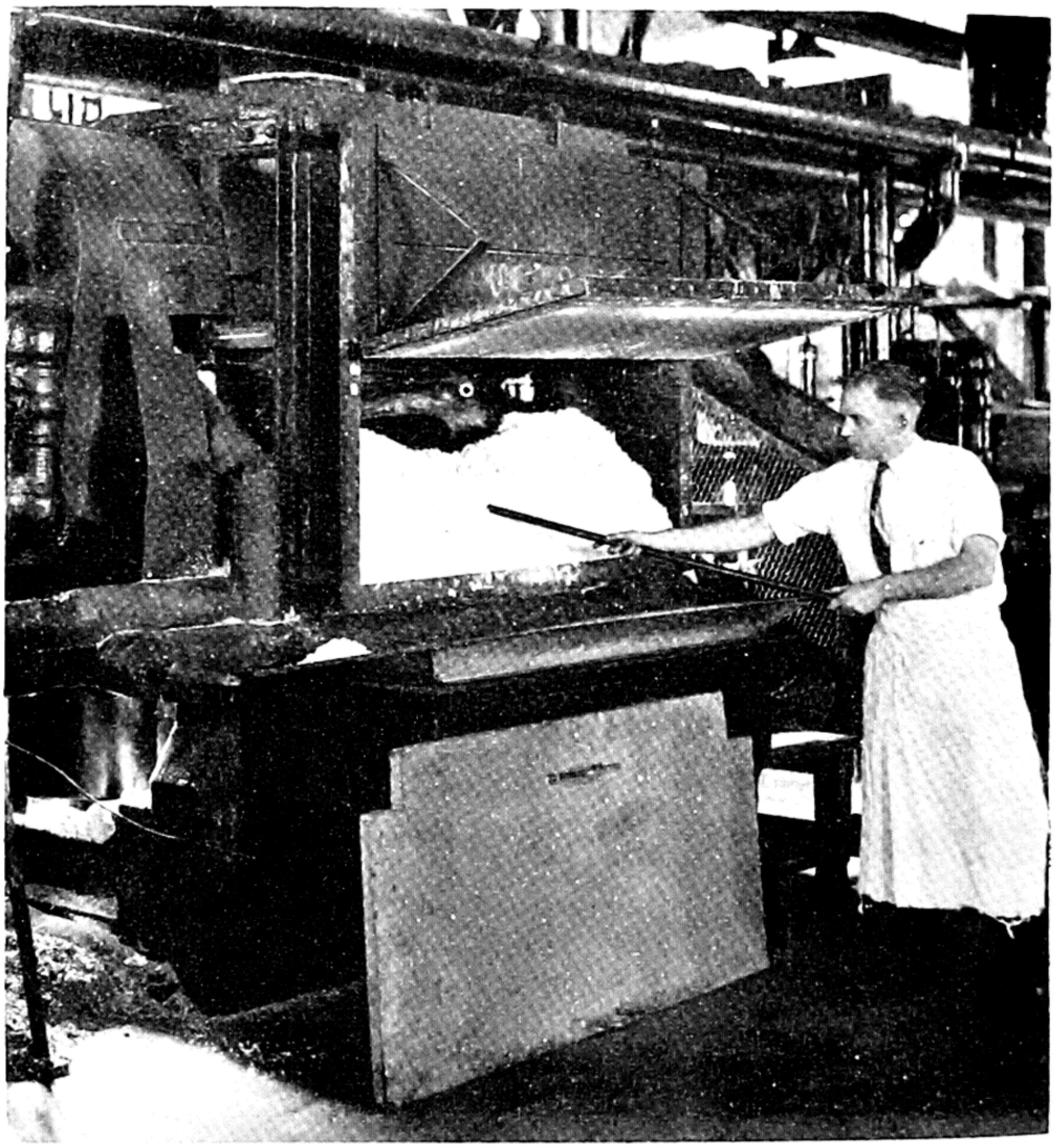


FIGURE 180.—The alkali cellulose shredder in a rayon plant. (Courtesy of E. I. du Pont de Nemours and Company, Inc., Rayon Department.)

This process is based on the discovery made in 1892 by two English chemists, Cross and Bevan,[4] that mercerized, or alkali, cellulose forms a definite, though unstable, compound with carbon disulfide. This compound, called cellulose xanthate, is a yellow solid and its formula may be written:

$$\underset{\textit{Alkali cellulose}}{\text{(Cellulose)}\,.\,\text{ONa}} + CS_2 \longrightarrow \underset{\textit{Cellulose xanthate}}{SC{<}\begin{matrix}\text{O}\,.\,\text{(Cellulose)}\\ \text{S}\,.\,\text{Na}\end{matrix}}$$

[3] Chapter 21.
[4] The first patent for this process was Brit. Patent 8,700 (1892).

Cellulose xanthate is soluble in dilute caustic soda and from this solution the regenerated cellulose is precipitated by the action of an acid. Simply stated, the chemical reactions of this process are as follows: Alkali cellulose is combined with carbon disulfide, and the resultant is dissolved in dilute caustic soda, producing a viscous solution called viscose. This solution is then sent to the spinning device and the emerging fine streams of the solution are coagulated by a bath containing sulfuric acid and other chemicals. A more detailed description of the process follows:

Sources of Cellulose. The sources of cellulose for this process are either wood pulp or refined cotton linters pulp. The American viscose rayon

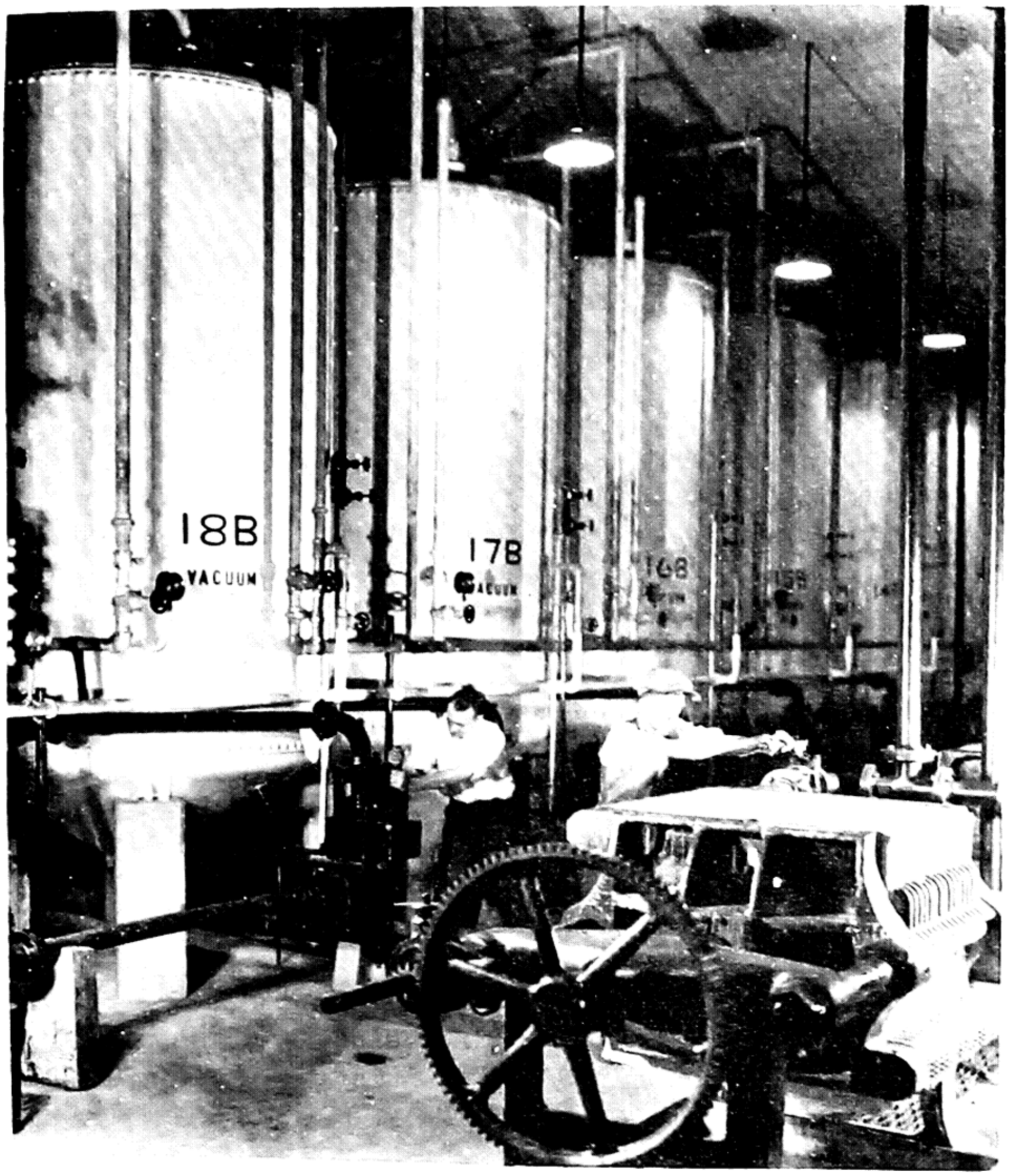


FIGURE 181.—The tanks in which the viscose is stored, aged, filtered, and liberated from bubbles by applying a vacuum. (Courtesy of E. I. du Pont de Nemours and Company, Inc., Rayon Department.)

industry at present depends more on wood pulp than on cotton linters pulp for its cellulose supply. The alpha-cellulose content of wood pulp for this process ranges from 88 to 92 per cent. Especially refined cotton linters pulp approximates 98 per cent alpha-cellulose content. Wood pulp and cotton linters pulp arrive at the rayon-producing plant in bales of white sheets. The sheets of pulp are stored in pulp storage rooms and held for several weeks in an atmosphere of controlled temperature and humidity.

Alkali Cellulose. When ready to be put into process, the pulp is carefully selected for steeping, which is merely a mercerization process. The pulp is placed in a steeping press which is then filled with a NaOH solution of 17 to 18 per cent concentration at a definite temperature. The pulp is allowed to soak for about one hour. In this stage of the process the α-cellulose remains insoluble, but the β- and γ-cellulose are leached out by solution with the caustic soda. The sheets of cellulose are then pressed together by a hydraulic ram to squeeze out the caustic soda, which is drained out of the tank. The resulting product is called alkali cellulose. The liquid drained out of the storage tank is sent to dialyzers for purification and reuse.

The soft alkali cellulose sheets are then dropped into shredder machines where the alkali cellulose is reduced to soft crumbs by a shredding operation which loosens, blends, and fluffs up the cellulose fibers. During the entire shredding operation the alkali cellulose is kept under a temperature of 18 to 20° C. (64.4 to 68° F.). The fluffy, white crumbs are removed from the shredder and dropped into rectangular steel compartment cans with reentrant separating spaces for maximum air contact. The containers are held in a temperature-controlled aging room for a period of several days. While aging, the alkali cellulose is oxidized and the length of the polymeric chain is reduced. It is the aging step which governs the viscosity of the final viscose solution.

Xanthate. The properly aged alkali cellulose is converted in the next step into another chemical compound, cellulose xanthate, by treating it with carbon disulfide for several hours under controlled temperatures. The xanthation is performed in a churn (baratte) which rotates around its horizontal axis while the carbon disulfide is introduced. As the latter is absorbed by the cellulose the color of the cellulose changes from white through gradations of yellow to orange. When the latter color stage has been reached, the xanthating process is completed. The excess carbon disulfide vapors are drawn off and the xanthate discharged into a viscose mixer or dissolving machine.

Spinning Solution Preparation. The dissolving machine is filled with dilute caustic soda before receiving the charge of xanthate. The latter is dissolved in the NaOH liquor and the resulting solution contains about 7.25 per cent cellulose and 6.5 per cent sodium hydroxide. It is brownish-green in color and viscous in character; hence the name "viscose."

If no delustering agents are added, this solution will be used for spinning bright viscose yarn. For dull and semi-dull yarns there is added at this stage a dispersion of titanium dioxide whose average particle size by surface mean is 0.56 micron. This delusterant becomes an integral part of the

yarn and, therefore, is permanent; it can never be rubbed out or washed off. Delustering by this method is possible because titanium dioxide has a greater refractive index than that of the regenerated cellulose.

The viscose solution is then filtered to remove any foreign matter and undissolved cellulose, and pumped through a series of storage or ripening tanks. In the last one or two of these, the viscose is placed under a vacuum for removal of trapped air, or else it passes through a system of continuous deaeration. The viscose solution is matured for several days under strict temperature control, *i.e.*, 16° C. (61° F.). The longer the viscose ripens, or the higher the temperature during ripening, the more readily does it flocculate

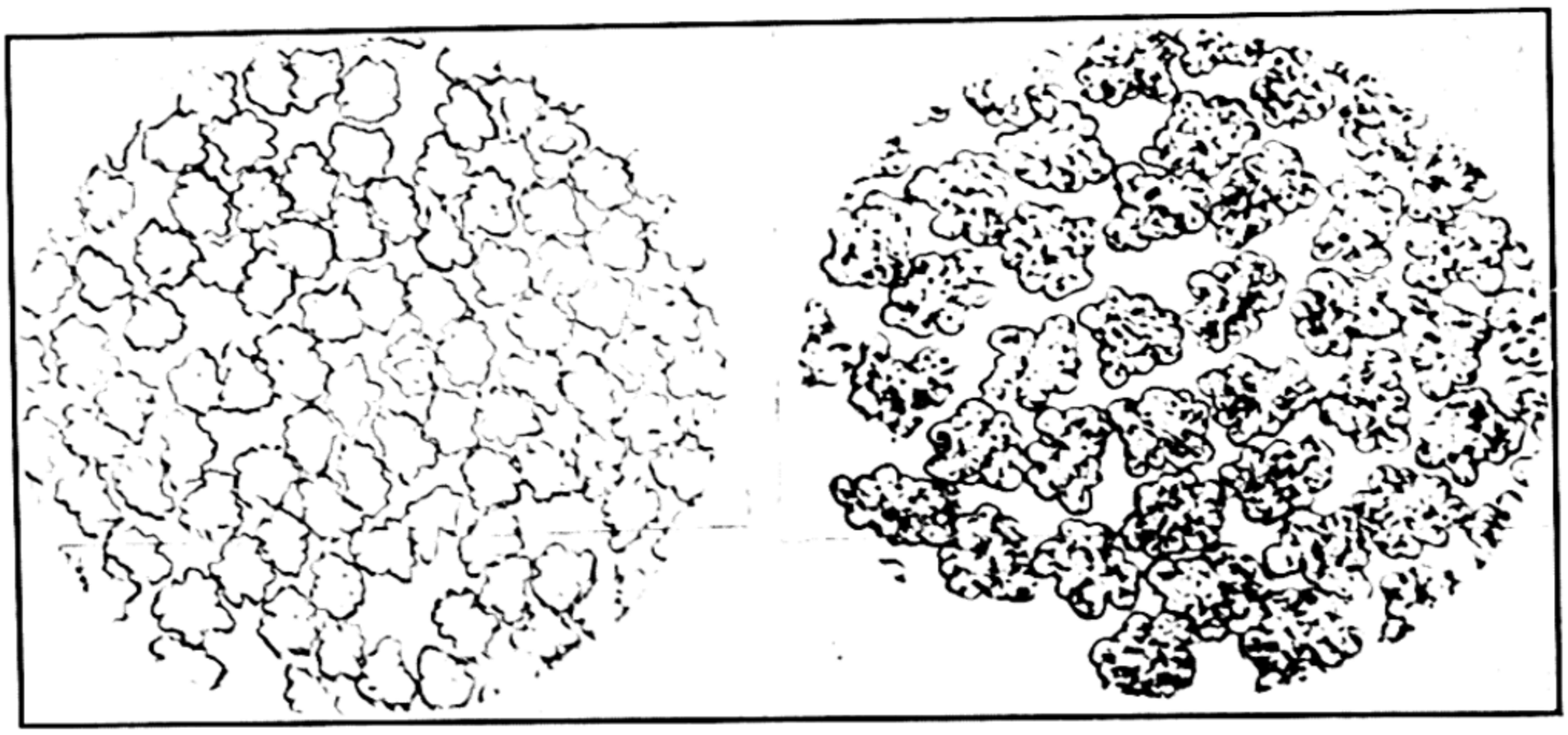


FIGURE 182.—Photomicrographs of a cross-sectional slice of the rayon thread, showing the several filaments, for a clear viscose (left), and for a delustered one (right). Courtesy of the Research Laboratory, Technical Division, Rayon Department, E. I. du Pont de Nemours and Company, Buffalo.

and the lower the salt index. The viscosity-time curve has a sharp break, and the aim is to spin the viscose when it is at exactly the right viscosity, that is, just before the break of the curve.

To test the degree of ripening of the viscose, one drop is placed in a salt solution, and its coagulation observed. The salt solution is made up of x cc of a concentrated stock solution of sodium chloride and $10-x$ cc of water; the resulting 10 cc are diluted with water to make a total of 40 cc. The value of x is changed in successive tests until the concentration of the salt solution is found which just causes the viscose to coagulate. This value of x is the salt index. The test consists in adding the drop of viscose to the 40 cc in an Erlenmeyer flask and shaking the flask in standardized fashion. The drop of viscose in the correct state of ripening divides into three flocks. A viscose which requires more salt than customary for proper coagulation is not ripe enough, and generally is held in the ripening room for an additional period. The salt index standard is generally about 4.0.

Among the several other methods for measuring the degree of ripeness, the Hottenroth Index method involves a titration with a 10 per cent ammonium chloride solution; it is more sensitive than the salt index method.

Variation in ripeness of the viscose when spun causes non-uniformity in a number of physical properties, such as tensile strength, stress-strain characteristics, spinning properties and dye acceptance of the resulting yarn. For a short time the properly aged solution may be preserved unchanged, in the right state for spinning, by setting the temperature at 0° C. (32° F.). It is customary to mix several batches of viscose in a blender.

Spinning and Coagulation of Viscose Solution. Conversion of the cellulose solution to a textile fiber is accomplished in the spinning operation. The viscose solution is pumped to the spinning machine and delivered to the spinneret, which may be described as a small nozzle containing many minute holes. Each spinneret is served by its own individual pump, and the viscose is under pressure. The spinneret is immersed from the beginning in a spinning or coagulating bath into which the fine streams of viscose solution are extruded. A typical spinning bath is composed of warm water at 40 to 45° C. (104 to 113° F.) containing 8 to 10 per cent of sulfuric acid, 13½ to 20 per cent of sodium sulfate, approximately 1 per cent of zinc sulfate, and from 4 to 10 per cent of glucose. The spinning bath may contain a small amount of a cation-active agent which serves to lessen clogging of the openings in the spinneret.[5] When the viscose solution, comprised of about 7.25 per cent of cellulose and 6½ per cent of caustic soda, enters this bath, the fine streams of viscose coagulate instantly.

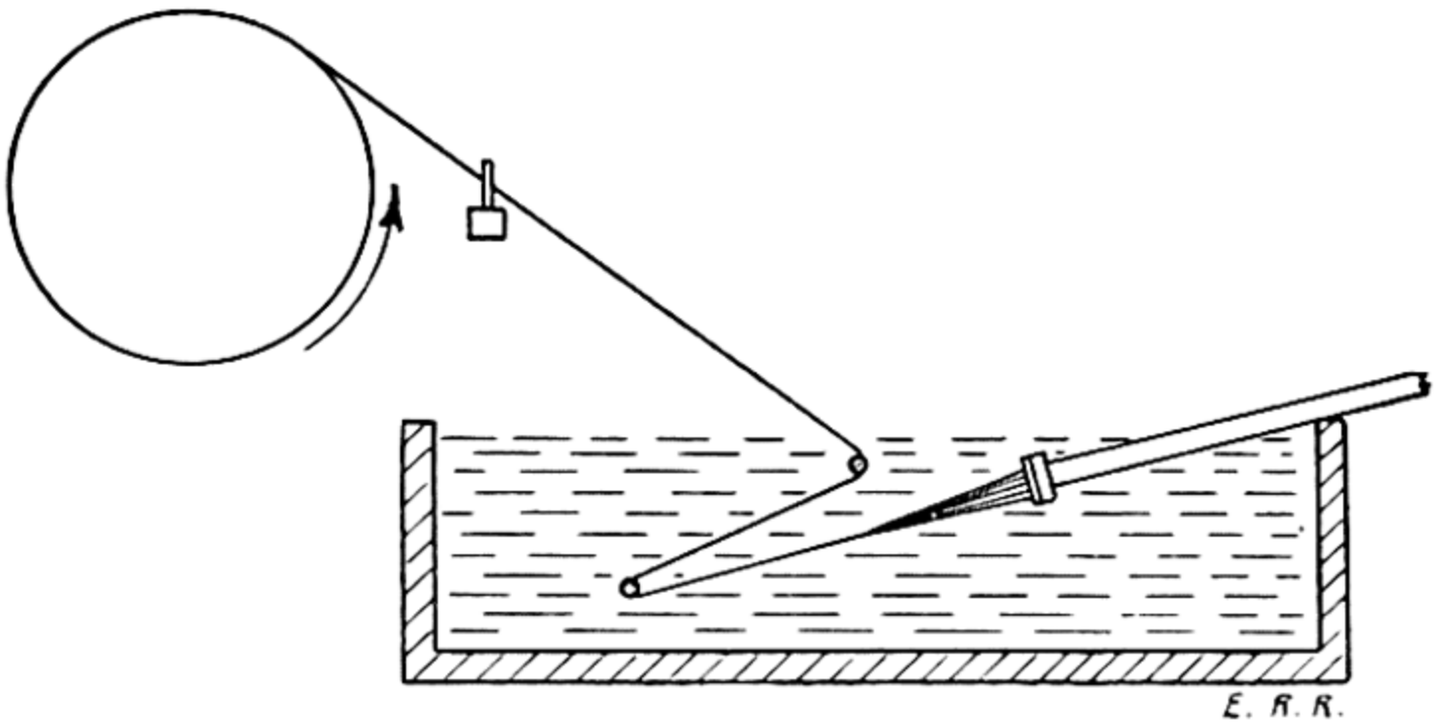


FIGURE 183.—A spinneret for viscose rayon.

The action of the acid in the coagulating bath is to regenerate the cellulose, to form sodium sulfate with the caustic, hydrogen sulfide with much of the sulfur, and carbon dioxide with the carbonate, as shown in the reactions below. The trithiocarbonate included in the reactions is due to a side reaction in the baratte ($CS_2 + Na_2S \rightarrow Na_2CS_3$). The gases are carried off by suction in the hoods overhead.

$$2\ (\text{Cellulose})\cdot O\cdot \underset{\displaystyle S}{\overset{\displaystyle \|}{C}}\cdot SNa + H_2SO_4 \rightarrow 2\ (\text{Cellulose})\cdot OH\ (\textit{regenerated cellulose}) + Na_2SO_4 + 2CS_2$$

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

$$Na_2CS_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2S + CS_2$$

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + H_2O$$

$$Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S$$

[5] U. S. Patent 2,125,031, July 26, 1938, to J. J. Polak and J. G. Weeldenburg. The patent mentions dodecylpyridinium chloride as a suitable cation-active agent.

If sodium sulphite is present, which is rare, elemental sulphur is formed:

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2, \text{ and}$$
$$SO_2 + H_2S \rightarrow 2H_2O + S.$$

The composition of the bath is kept constant by rapid circulation to a large supply tank. There are three factors which bring about unbalance in the bath: (1) loss of acid, (2) gain of water, and (3) gain in sodium sulfate content. In order to restore balance, fresh sulfuric acid is fed into a correcting tank; periodically portions of the bath liquor are withdrawn to lead-lined evaporators and there concentrated; the concentrated liquor is cooled, and the Glauber salt which separates removes the excess sodium sulfate. The yarn passes through the spinning bath at the rate of 70 to 100 meters per minute.

There are modifications of the coagulating bath composition of which one is indicated in reference 6.

Systems of Spinning. Three systems of spinning viscose yarn are in use today in the United States—the pot, bobbin, and continuous processes. In the pot system the yarn passes horizontally through the spinning bath and up over a rotating wheel called a "Godet Wheel" and down into a centrifugal pot where the entering yarn is coiled by centrifugal force on the wall of the pot. This pot, about 7 inches in diameter, is rotated at from 6000 to 10,000 rpm. The revolution of this pot causes individual filaments to be lightly twisted into a yarn—2½ turns per inch—and in addition throws off, through perforations in the wall of the pot, much of the spinning bath solution which saturates the yarn. When a pot is filled, which usually takes several hours, the cake (about 1 pound) is doffed and removed from the spinning machine. The yarn undergoes several finishing processes, described later, before reaching its final state.

In both pot or bobbin systems, the spinning may be either horizontal or vertical. In the bobbin system with vertical spinning, for example, the yarn is wound on a perforated bobbin located directly over the coagulating bath; the viscose solution is ejected vertically upward into the spinning bath and out of the solution. It should be noted that in the bobbin spinning system, no twist is imparted to the filaments; twisting is done in a later operation. The yarn, after spinning, undergoes subsequent purification treatments similar to those given to yarn spun by the pot system.

An especially valuable continuous filament rayon is manufactured for making the cord for the heavy truck and bus pneumatic rubber tires. A spinneret with 500 openings, for example, delivers viscose to the spinning bath; the filaments are united, washed, passed over several pulleys of which one rotates fast, so that the thread is stretched. Any method of spinning is suitable; it is the stretching which is important. After drying, the thread is wound on the usual small spools.

Later a number of small spools are unreeled on a suitable machine and the threads united and spooled on a large horizontal spool, 4 feet long. The large spool or "beam" is shipped to the cord-weaving establishment. The rayon for tire cord is especially strong (see table). Its importance is shown

[6] *Ind. Eng. Chem.*, 22, 464 (1930).

by its production figure. In 1947, viscose filament yarn totalled 515 million pounds, divided into 290 million pounds of textile yarn, 225 million pounds tire yarn. About 50 per cent of the cord requirement of the tire manufacturers was rayon.

TABLE 74.—*Comparative strength of different fibers.**

	Tensile strength Per denier	Elongation to break (%)
Wool	dry, 1.2 gram	20-25
Acetate rayon	1.3	22-28
Viscose rayon	2	14-18
Cotton	2.7 to 4.8	4-10
High tenacity tire cord viscose rayon	3.5	9-12
Silk	3.5	20-25
Nylon	4.5	15-25
Sisal hemp	up to 8.0	3- 5

* From various sources.

The newest spinning system is the "continuous" process, whereby the yarn passes from the spinning bath, located at the top of the spinning machine, down over a series of rotating thread-advancing reels. Each thread passes over 10 reels which are mounted stepwise one below another, and each represents a stage in the processing of the yarn. At the bottom of the *continuous spinning machine*, the yarn is dried and run onto the final bobbin as finished yarn. The complete operation from the spinning bath through all the washing, chemical treatments, finishing, drying, and twisting takes only about 4½ minutes.[7]

Finishing of Pot and Bobbin Yarn. Unlike the continuous process, the yarn spun by the pot or bobbin system must be treated and finished in special operations after leaving the spinning machine. These after-treatments consist of washing, desulfuring, bleaching, oiling or "finishing," drying and packaging.

The cake or bobbin removed from the spinning machine is washed in warm water. The cake may be washed as such, or reeled into skeins before washing; the bobbin yarn is washed on the bobbin. The yarn may be dried, and desulfured by passing it through an alkaline sodium sulfide solution, and washing in water. There follow bleaching with sodium hypochlorite, washing, and oiling or "finishing," which is done by treatment with a solution of a soluble oil, or with a soap solution. The finishing treatment pro-

TABLE 75.—*Prices for viscose spun rayon by deniers, December, 1947.**
(Regular tenacity)

					Per pound
75	deniers	30	filaments	Cones	1.07
100	"	40	"	"	.94
125	"	40	"	"	.83
150	"	40	"	"	.74
450	"	100	"	"	.55

* "Rayon Organon."

[7] "Rayon, mile by mile, perfect, inch by inch," illustrated descriptive publication, Industrial Rayon Corporation, Cleveland, O.

tects the rayon yarn in later textile operation. A final washing precedes drying, which is followed by winding on cones, cops, tubes, or in skeins, all of which are then inspected, graded, sorted and shipped.

A few more words regarding filaments and deniers are in order. For a given denier, the higher the filament number, the softer the yarn and fabric to the touch (the yarn is a group of filaments). For yarn in general, the higher the denier, the lower the price per pound, as shown in Table 75.

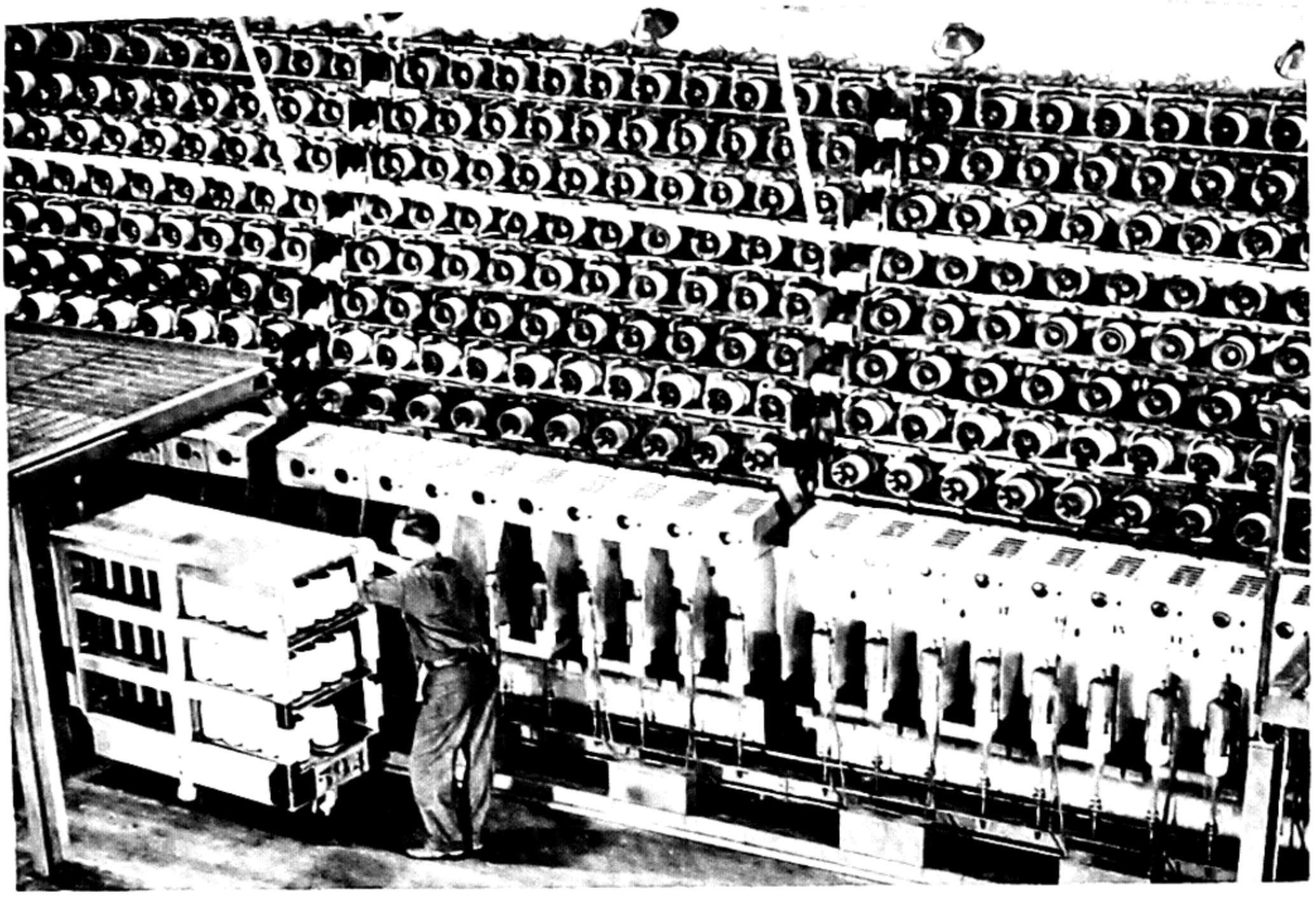


FIGURE 184.—A view of the continuous spinning machine for continuous filament rayon production. (Courtesy of Industrial Rayon Corporation, Cleveland, Ohio.)

Thick and thin yarn, to mention one of many specialties and novelties, with irregular variations in thickness, is produced by using two pumps, one a uniform speed pump, one with variations in speed which are all different.

Raw Material Consumption. The approximate poundage consumption of raw materials per pound of viscose-process rayon yarn is as follows: wood pulp and cotton linters, 1.15 to 1.25; caustic soda, 1.4; carbon disulfide, 0.35; sulfuric acid, 1.7 to 1.9; glucose, 0.5; and all other chemicals, 0.4. In addition, from 100 to 200 gallons of pure water are required to produce one pound of viscose rayon yarn. These figures represent gross consumption of these chemicals and do not take into account any recovery thereof.

Acetate Rayon. The acetate process of rayon yarn manufacture ranks second only to the viscose process in volume of production. United States production of acetate yarn in 1947 amounted to 30 per cent of the total rayon yarn output. The principal raw materials used by this process are refined cotton linters, special high alpha dissolving wood pulp, acetic

anhydride, glacial acetic acid, sulfuric acid, acetone, titanium dioxide, and water.

This process is based on the original work of Naudin and Schutzenberger in 1865, although the full development of this process on a commercial scale did not come about until after World War I under the direction of Henri and Camille Dreyfus. Since the early twenties its growth has been extremely rapid, both here and abroad.

The following are the general principles and stages of operation in the manufacture of acetate yarn.

Acetylation. The first operational step in this process is the acetylation of the cellulose. Batches of cotton linters or wood pulp which have been pretreated with acetic acid, or some other activating chemical, are placed in an acetylator, previously charged with a solution containing a mixture of acetic anhydride and glacial acetic acid, together with a small quantity of concentrated sulfuric acid as a catalyst.

The pretreated cellulose is gradually added to this charge with constant mixing. During the period of acetylation the temperature of the solution is rigidly controlled and the reaction is carried to completion, that is, to a degree of acetylation approximating the tri-acetate which dissolves in the acetylating mixture. In the final stage of acetylation the solution is a heavy, viscous, semi-transparent, acrid-smelling fluid and is commonly called primary acetate.

Hydrolysis of Primary Acetate. The second step is the hydrolysis of primary acetate into secondary acetate. In this operation a solution of primary acetate in strong acetic acid is partially diluted with water, and then allowed to stand for some time at increased temperatures, during which time the primary acetate is partially saponified (hydrolyzed) to the secondary or acetone-soluble state whose acetyl content approximates the diacetate.

When the reaction has reached the desired stage, the secondary acetate is precipitated by pouring the solution into a large tank of cold water. The secondary acetate is precipitated out in the form of white flakes. These cellulose acetate flakes are washed in warm water until free of acid, dried, and then stored in bins.

Spinning Solution Preparation. The spinning solution is prepared by dissolving these cellulose acetate flakes in acetone. The preparation of this spinning solution is done in a closed mixer into which the cellulose acetate flakes and the acetone are added in the proper proportions and gradually mixed together. From 12 to 24 hours are required to dissolve the cellulose acetate completely. In the final spinning solution the cellulose acetate content may range from 15 to 30 per cent. For dull luster yarns a small amount of titanium dioxide is introduced into the solution during the mixing period.

From the mixer the solution is run into tanks where several batches of the solution are blended. The contents of these blending tanks are then filtered several times, and finally the solution is drawn into storage tanks where all air bubbles are removed. The solution then is ready for spinning.

Spinning Acetate Yarn. Acetate yarn is spun by the dry spinning system as contrasted with the wet spinning system used in the viscose and cuprammonium processes of yarn manufacture. In this dry method of spinning, the spinning solution is delivered from storage tanks to the spinneret on the spinning machine, through which the solution is forced downward under controlled pressures into an enclosed spinning chamber. The spinning solution emerging from the spinneret is met by a rising current of warm air which evaporates the acetone. By the time the acetate filaments have reached the bottom of the spinning chamber, coagulation has been completed and the filaments dried. From a chemical standpoint, the process is now completed. It is only necessary to twist the filaments and package the yarn for shipment, or, if staple fiber is being made, to cut the filaments to the desired lengths, bale and ship. Trade names are "Acele," "Celanese," and others.

Raw Materials Used. In producing a pound of acetate rayon the pounds of raw materials required are approximately as follows: Refined cotton linters, 0.70; acetic anhydride, 2.40; glacial acetic acid, 6.00; sulfuric acid, 0.07; acetone, 4.00; titanium dioxide, 0.02; as well as about a thousand gallons of water.

These figures represent gross consumption and do not take into account the recovery of any of the chemicals used. Because of the initial high cost of the chemicals consumed by this process, efficient recovery systems have been developed without which this process would be commercially and economically impracticable. It is because of the development of remarkably efficient recovery systems for such chemicals as acetone and acetic acid [8] that the price of acetate rayon to the consumer has been constantly lowered over the years.

Cuprammonium Process. The cuprammonium process of rayon yarn manufacture is the third method of production. The quantity of yarn produced by this process in the United States today is small by comparison with the output of the viscose and acetate processes. This process of manufacture has, nevertheless, been an important factor in the rayon yarn industry in this country since 1926.

In this process of manufacture, purified cotton linters are commonly used as the principal source of cellulose, although in recent years this process has been experimenting with special grades of high-alpha wood pulp. Before processing, the purified cotton linters are cleaned by cooking in a mild caustic solution under pressure and then are bleached. These linters, then essentially 100 per cent pure alpha-cellulose, are mixed with basic copper sulfate and ammonia aqua of 28 per cent ammonia. This solution must be prepared under rigid chemical control to obtain a solution of the proper viscosity and cellulose content. The solution is then filtered and stored in tanks.

The solution, when used, is carried to the spinning machines and spun by the stretch spinning device. By this method, the spinning solution is pumped through spinnerets into a glass funnel through which de-aerated water flows. On the way through this funnel the single filaments are stretched and slowly solidified, the water meanwhile extracting most of the

[8] See Brewster process, Chapter 16.

ammonia and part of the copper. On leaving the funnel, the filaments pass through a bath of mild sulfuric acid which fully coagulates the filaments and at the same time extracts more of the remaining copper. The filaments are then wound on reels in the form of skeins. These skeins are sprinkled with plain water, removing any of the remaining acid and copper sulfate, after which the yarn is washed in a soap bath, dried, and then treated with a second soap bath to soften up the yarn, and dried again. The yarn is packaged on cones, bobbins, or any other form desired and shipped to customers.

The importance of these various processes of yarn and staple fiber manufacture in the United States is shown in the following table.

TABLE 76.—*Production of rayon by processes for the United States in millions of pounds**

	Filament yarn		Staple rayon and tow		Total
	Viscose and cuprammonium	Acetate rayon	Viscose rayon	Acetate rayon	
1946	491.2	186.3	132.7	43.7	853.9
1947	525.2	221.3	168.2	60.2	975.1

* "Rayon Organon."

The rayon yarn industry in the United States has reached an impressive size, as indicated by these figures.

Rayon Staple Fiber

Rayon staple fiber has been one of the outstanding developments in the rayon industry especially over the past decade. Although this rayon product was originally developed in Germany during the war of 1914-18, it made no appreciable progress until the late twenties. Since that time, however, its growth has been extremely rapid. In 1929 world rayon staple fiber production amounted to a little over 7 million pounds; by 1940 world production totaled 1237 million pounds. Of this 1940 world output Germany produced 575 million pounds, Japan 300 million pounds, Italy 225 million pounds, United States 81 million pounds, and all other countries 56 million pounds.

The world production of staple rayon fiber reached a high in 1942, with the figure of 1,537 million pounds, of which 153 million pounds was produced in the United States. The latter figure rose to 224.1 million pounds in 1947, whereas world production dropped to below 1,000 million pounds.

As has been previously pointed out, rayon filament yarn is composed of a number of fine, continuous rayon filaments grouped and lightly twisted together. On the other hand, rayon staple fiber is made by cutting continuous rayon filaments into short lengths. These short fibers are baled by the staple fiber producer and shipped to cotton, woolen, worsted, or silk spinners to be spun into a yarn commonly known as spun rayon yarn.

Methods of Manufacture. Rayon staple fiber is made principally by the viscose process, although increasing amounts are being manufactured by the acetate process. In the production of staple fiber the chemical stages in the manufacturing process are essentially the same as those for filament yarn,

as previously described; that is, the raw cellulose material is chemically treated in such a way as to put the cellulose into a solution for spinning into filaments.

In the viscose process of manufacture the difference between filament yarn and staple fiber production takes place at the spinning and not at the chemical preparation stage, as noted. As previously brought out in this chapter, in the spinning of rayon yarn the filaments are collected on bobbins or in centrifugal pots and periodically doffed. In the manufacture of staple fiber these operations do not exist. Instead, the filaments from each spinneret are carried along to the end of the spinning machine to form a continuous "tow" or "rope" of filaments.[9] Moreover, in comparison with the relatively small number of holes in the spinneret used in the spinning of filament yarn, the number of orifices in the staple spinneret is substantially greater, for example, instead of 40, or 100, it is of the order of 5000 or more.

The "rope" requires additional processing before it reaches the finished state. It may be immediately cut to the desired staple lengths and subsequently washed, desulfured, bleached, and dried; or the uncut "rope" may be desulfured, washed, bleached, and dried before being cut into staple lengths. Furthermore, the tow may be sold in that form (uncut) and it can then be made into spun rayon yarn by methods which are simpler than the worsted and schappe spinning systems. The system of cutting the wet tow into staple lengths is called the wet cut system, and cutting the dry tow, the dry cut system. Regardless of the method of cutting, however, these short fibers in the final finished state are called rayon staple fiber. They are then baled and shipped to the customer. The bale weighs in the neighborhood of 500 pounds.

Likewise, in the acetate process of staple fiber production, the chemical preparation is the same as that for the continuous filament acetate yarn. Unlike the viscose process, however, it is possible to produce acetate staple on continuous filament acetate yarn spinning equipment, although acetate staple is also produced on specially developed rayon staple fiber spinning machines. The acetate filaments are dry cut into short lengths and sold to textile spinners for spinning into yarn.

Types of Staple Fiber. Inasmuch as rayon staple fiber must be spun into yarn by the cotton, wool, worsted, and schappe (spun silk) systems of yarn spinning, it is necessary for rayon producers to supply this fiber cut into suitable lengths. Therefore, rayon producers cut rayon tow into varying lengths as determined by the system of yarn spinning for which the fiber is intended. For the cotton system the fibers are generally cut from 1¼ to 2 inches long. Lengths of about 3 to 4 inches are usually required by the woolen system, and lengths of 5 inches and over are used by the worsted and schappe spinning systems.

Similarly the denier range of the individual filaments may be varied by the rayon producer according to the customer's needs. The commercial range, at present, is from 1¼ to 20 denier per filament. Staple fiber is made in both bright and dull lusters.

[9] Strictly speaking, the filaments coming off the spinning machine and gathered close form the rope, and the rope, when purified and dried, becomes tow.

Tow is bought to a growing extent for the production of "*flock*," which consists of short lengths, of the order of 0.020 to 0.1 inch, used by textile and paper converters to produce suède pile and napped effects on fabric and wall papers. Matted together with a binder, flock forms a cloth which does not require weaving (tea-bags, bandages, throw-away diapers).

The principal consumer textile products made of spun rayon yarn are apparel fabrics for men's and women's wear. This rayon product also has growing markets in such household products as blankets, rugs, draperies, diapers, etc. The current prices (Jan. 1948) of viscose and acetate staple fibers are 37 and 50 cents per pound respectively for the basic grades.

Aside from rayon yarn and rayon staple fiber, there are two other important products made by the rayon industry. These are bands and strips of rayon less than one inch wide and monofilaments of rayon. In this classification of narrow bands and strips may be included the item of artificial straw. In the monofilament category are included those single heavy deniers of rayon filaments spun from a circular orifice. This product is often referred to as artificial horsehair.

An *artificial wool* is made by dissolving casein in alkali, forcing the solution through large-holed spinnerets, and coagulating the threads in an acid bath; "Lanital," ("Aralac," "Aratex").

Nylon

Nylon yarn is a new synthetic fiber now available in commercial quantities; it comes closer to silk in constitution and properties than any other synthetic fiber previously manufactured. In 1946, the seventh year of its commercial availability, the annual production reached 24 million pounds. Nylon is already well known to the general public because it has gone into a considerable volume of nylon hose and other articles of wearing apparel.

Nylon is a generic name applied to all superpolymers made from long-chain dibasic acids combined with long-chain diamines. Nylon 66 is the specific nylon now made on a large scale; it is the superpolymer formed by the combination of adipic acid and hexamethylene diamine. These two substances, both solids at room temperature, are mixed in solution to form nylon salt. Stabilizing agents are added to control molecular weight and viscosity; the solution is evaporated, and the liquid residue transferred to an autoclave in which it is heated for many hours. The product is a melt, consisting of the final superpolymer. The melt is extruded in ribbon form onto a chilled wheel (casting wheel); the congealed ribbon, now a tough, horny material, is cut into small chips convenient for storage. To make the fiber, the chips are melted by passing them between heated grids; the liquid is fed to a pump and is supplied under the pressure of the pump to spinnerets, which form the filaments. The latter are congealed at once by a gentle blast of air, and wound on bobbins. Next, the primary filaments, rather useless in their existing form, are cold-drawn to about four times their original lengths, with a decrease in diameter. By this operation, their properties are changed completely, for now they form elastic fibers, transparent, lustrous, and of high tensile strength. The explanation for the change is that the original random

arrangement of the superpolymer molecules gives place to an oriented one. The cold-drawn filaments are twisted, sized, and rewound on spools or cones, ready for the textile mill.

Nylon fiber may be made into any of the standard deniers. The diameter of the individual filaments is governed by controlling the rate at which the molten nylon is pumped to the spinneret, and by the rate at which the filaments are drawn away. The filaments from one spinneret are united

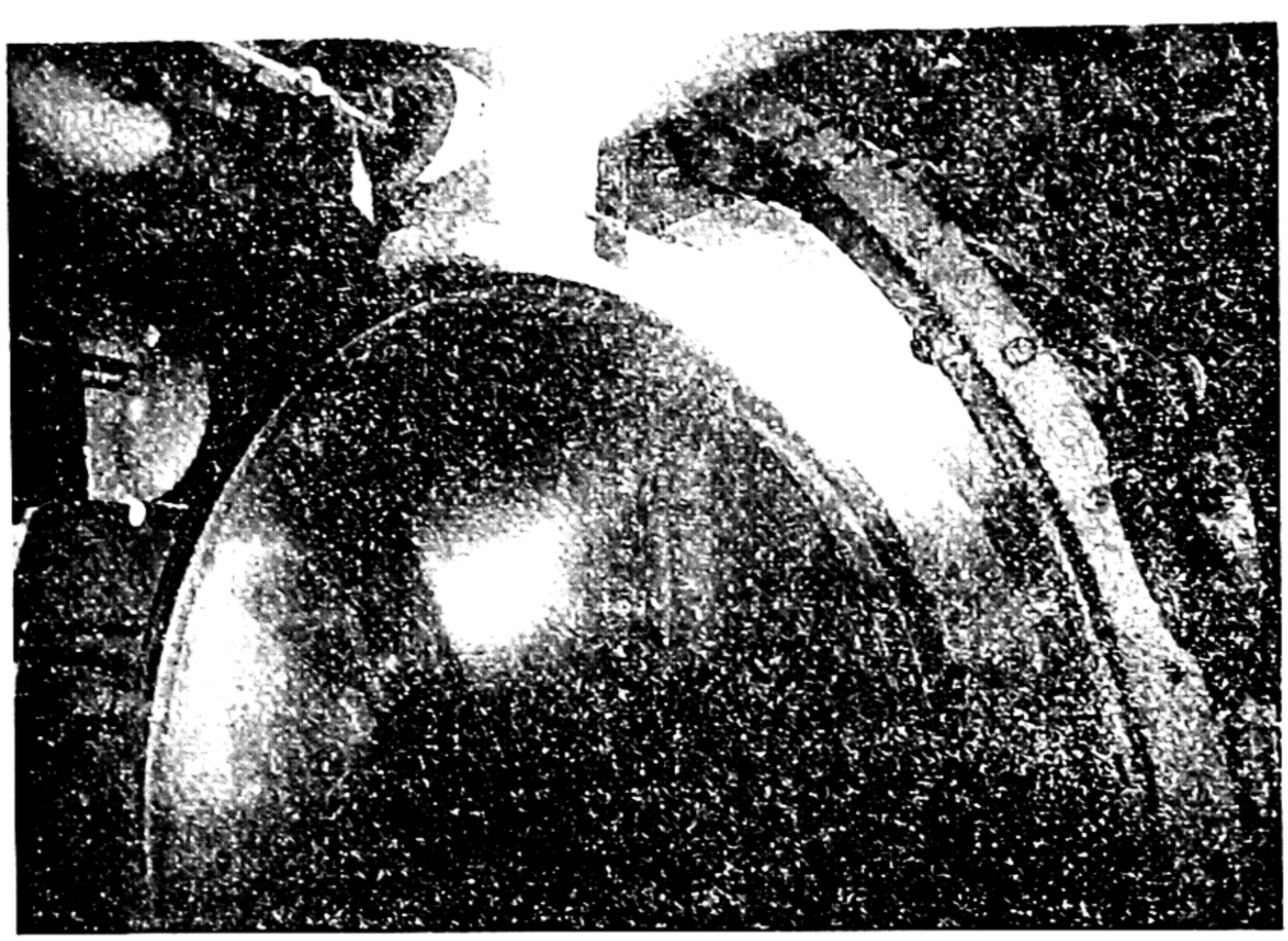


FIGURE 185.—The molten polymer is extruded from the autoclave onto a chilled wheel, the casting wheel here shown, forming a wide ribbon. A spray of water helps the mass to solidify. Nylon at this point resembles ivory. In later operations it is chopped, melted and extruded as filaments. (Courtesy of E. I. du Pont de Nemours and Co., Nylon Division, Wilmington, Del.)

to form the yarn; the number of filaments in the yarn is determined by the number of holes in the spinneret. Filaments of extreme fineness can be made from nylon, much finer than those of ordinary textile fibers.

The current nylon yarn list prices per pound (February, 1948) are as follows:

Denier	Filament	Price	Denier	Filament	Price
15	1	$5.50	30	23	$2.75
20	7	3.35	40	13	2.15
20	20	4.70	40	34	2.25
30	10	2.55	70	70	1.90

It is expected that before long, nylon staple fiber will be introduced commercially.

Nylon may be delustered as rayon is, by the addition of finely powdered (colloidal) titanium dioxide or similar pigments. Nylon may be colored

in the molten mass, or the yarn or finished fabrics may be dyed, preferably with acetate rayon dyes.

Nylon textile monofils are comparatively thick single filaments, and serve for making tooth brushes, paint brushes, insect screening, and for other purposes. Nylon solutions permit the coating of metal wires for insulation. Nylon molding powder is being developed for injection-molding equipment. Nylon fiber is used for shroud lines and canopies for parachutes, and for other military purposes.

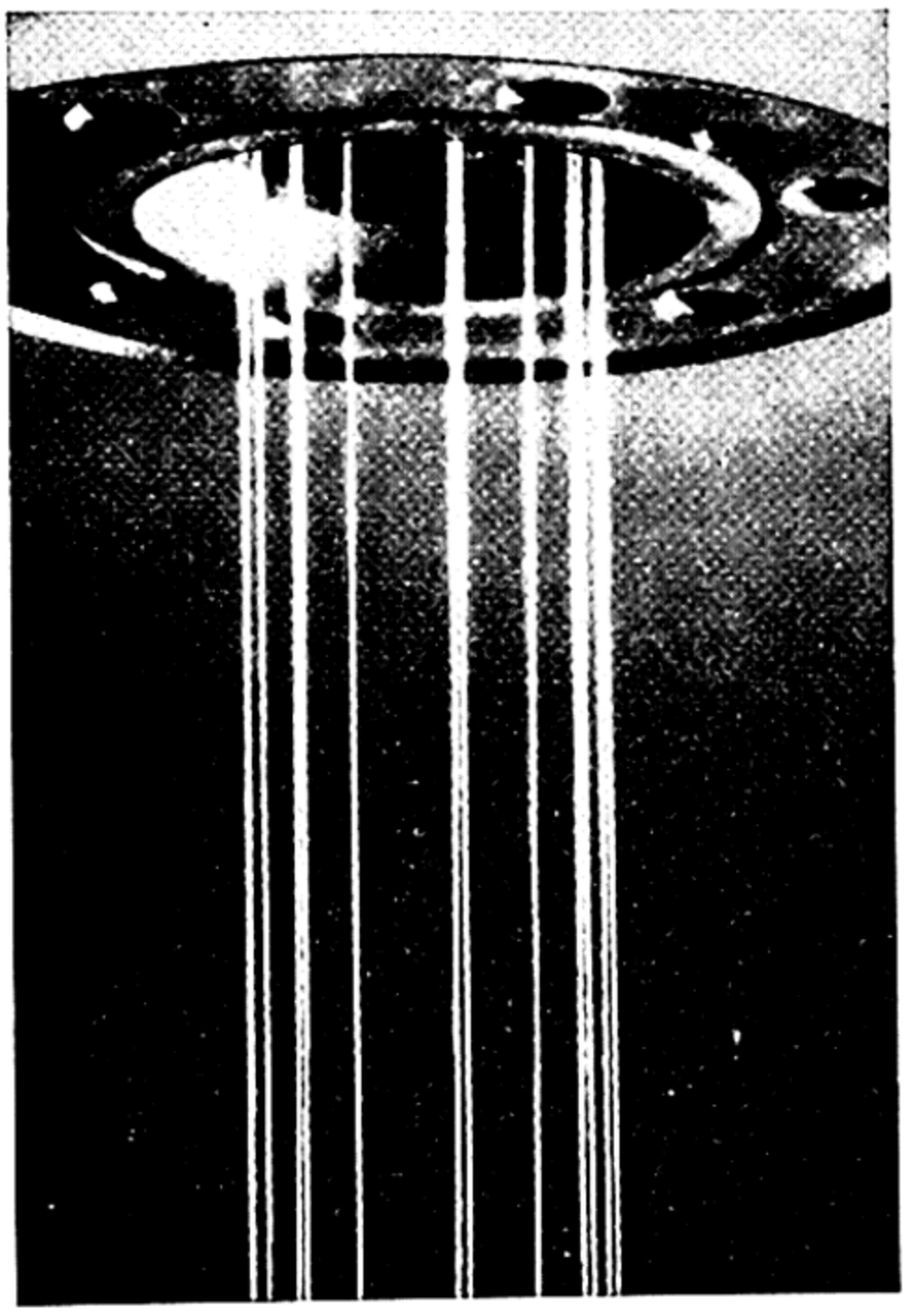


FIGURE 186.—Spinning the nylon yarn: the extrusion of molten nylon through a spinneret to form the filaments which become solid as soon as cool air strikes them. (Courtesy E. I. du Pont de Nemours and Co., Nylon Division, Wilmington, Del.)

Nylon is not soluble in water, nor in most of the ordinary organic solvents; it dissolves in phenol, cresol, and formic acid. The filaments may be dry-spun with such a solution, as acetate rayon is, but because of the nature of the solvents this is not desirable.

Nylon 66 melts at 263° C. (511° F.). The tensile strength is 4.5 to 7 grams per denier, dry, 4.0 to 6 grams, wet, depending on degree of molecular orientation and chain length; for comparison, a good silk has a tensile strength of 4.5 grams dry, and 3.8 grams wet.

The two raw materials for nylon 66 had to be manufactured by new processes, for until this development, adipic acid and hexamethylene diamine were not made commercially in this country. Adipic acid, $COOH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, is made from phenol. First, the phenol is hydrogenated to cyclohexanol, with the aid of a contact catalyst, at elevated temperatures. Next the cyclohexanol is oxidized, also catalytically, to give adipic anhydride, which is readily hydrated to the acid. Hexamethylene diamine is made from adipic acid by treating it catalytically with ammonia, to form the dinitrile, and hydrogenating the latter to give the final

diamine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, a solid at room temperature.

An alternate starting material is cyclohexane,[10] derived from petroleum; still another is furfuraldehyde.[11] From the latter are made in turn, furan, tetrahydrofuran, 1,4-dichlorobutane (by HCl), adiponitrile (by NaCN

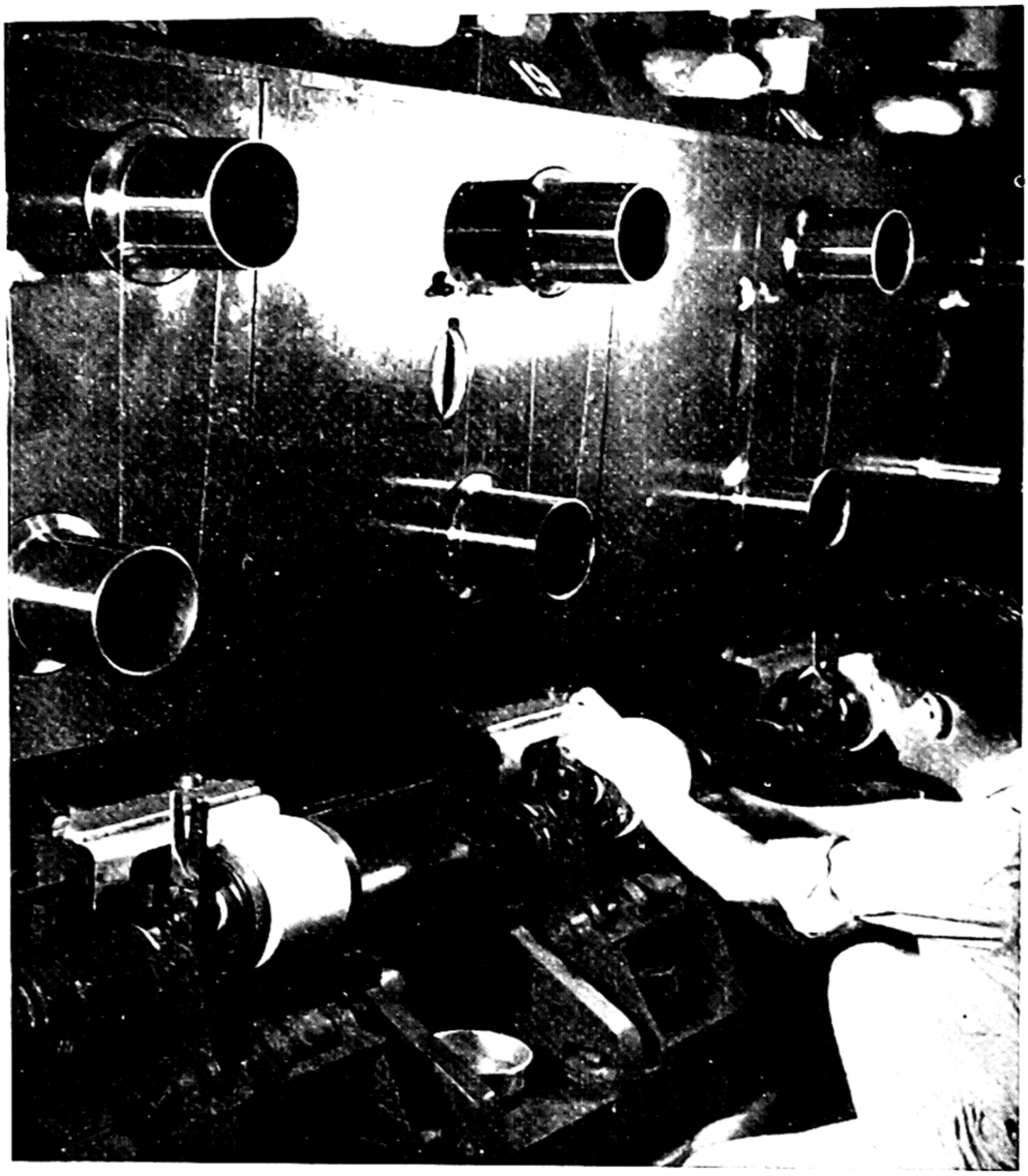


FIGURE 187.—Nylon yarn, formed by bringing together the fine filaments extruded from the spinneret, is wound on bobbins and sent on to the textile area of the plant where it is given various treatments similar to those accorded other fine yarns. (Courtesy E. I. du Pont de Nemours and Company, Nylon Division, Wilmington, Del.)

[10] *Chem. Industries*, 59, 470 (1946).

[11] "Oat hulls-Adiponitrile-Nylon," O. W. Cass, *Chem. Industries*, 60, 612 (1947). "Furfural formation and behavior," A. P. Dunlop, *Ind. Eng. Chem.*, 40, 204 (1948); "Chemistry of furans," G. F. Wright and H. Gilman, *ibid.*, p. 1517; "Catalytic hydrogenation of furan compounds," B. H. Wojcik, *ibid.*, p. 210; "Chemical intermediates from furfural," O. W. Cass, *ibid.*, p. 216.

reaction), adipic acid (by hydrolysis), and from adiponitrile again, hexamethylenediamine by hydrogenation. A large plant is about to go into operation for the production of adiponitrile. For the present, the nitrile will be converted into hexamethylenediamine; the adipic acid will be made as before, from cyclohexane, phenol, or a similar compound. The acid and the diamine are then made into nylon salt.

From furfural, by catalytic hydrogenation, tetrahydrofurfuryl alcohol is formed; by catalytic dehydration at 375° C. this becomes dihydropyran, a substance which yields heptamethylene diamine when carried through four steps in succession and, alternatively, pimelic acid ($HOOC \cdot (CH_2)_5 \cdot COOH$). These two substances are the starting materials for a new member of the nylon family.

The linear polymer forms by the combination of the end group of the acid with the end group of the diamine, leaving at each end of the new molecules reactive groups which undergo similar combinations. The first compound would be $COOH \cdot (CH_2)_4 \cdot CO \cdot NH \cdot (CH_2)_6 \cdot NH_2$.

Nylon in its several forms was indispensable to our armed forces in World War II. Unstretched, or partly stretched nylon in the form of rope for towing gliders was superior to all other materials because of its greater strength, its greater lightness, and its elasticity: as the pull came to the motionless glider, the stretch of the rope itself cushioned the shock, or "slowed the rate of loading." A rope could be used only once (generally). Nylon cloth for parachutes has become a byword. Laminated nylon flak suits provided protection for our Navy and Marine Corps airmen.

There are 12 different types of textile nylons being produced today.

The output of nylon is expected to be at the rate of 60,000,000 pounds per year at the end of 1948.

The following figures may be of interest in contrasting the various textile fiber consumptions:*

1946, cotton consumption	403.7 million pounds per month
1946, rayon total	70.1 million pounds per month
1946, wool	62.4 million pounds per month

Prices of the textile raw materials contrasted as follows:*

Late in 1947, viscose rayon staple was quoted at ..	34.2 cents a pound
Late in 1947, $\frac{15}{16}$ middling spot cotton	35.8 cents a pound
Late in 1947, wool, scoured	125.5 cents a pound

* For the U. S.; from "Rayon Organon."

Cellophane, Bottle Seals, Cellulose Sponge

Transparent sheets for wrapping objects (cellophane, "Transparit," "Sylphrap") are made by extruding a viscose solution through a long narrow slit which lies under the surface of the liquid in the coagulating bath. The slit is at the bottom of a correspondingly long, rather narrow hopper which contains viscose under pressure. The size of the slit, for example 0.004 inch, determines the thickness of the sheet and is adjustable by means of numerous hand-operated screws. The length of the slit, *e.g.*, 60 inches, determines the width of the sheet. The viscose is coagulated at once upon striking the bath, and forms a continuous sheet which travels by means of rollers into a number

of different baths in which the regenerated cellulose is washed, desulfured, bleached. The cellophane sheet passes through a bath of glycerin where it absorbs 18 per cent of its dry weight of glycerin, the softening agent. It may be dyed while still in the gel stage by passing it through a dye bath. The clear or colored sheet is then dried over steam-heated rollers and wound into rolls. The complete assembly is called the casting machine. The speed of formation may be as high as 200 feet per minute.

Cellophane is moisture-proofed by passing the sheet through a lacquer solution and lifting it, glass-enclosed, to a height of 50 feet or so. As the sheet rises, a current of warm air vaporizes the solvents, which are recovered by means of activated carbon. The sheet finally reaches a roller where it turns and travels down through a cooling and moistening chamber, to be finally spooled again, ready for cutting into flat sheets of various dimensions.

Bottle seals are short, cylindrical bands of regenerated cellulose in the moist state, with or without trade marks or lettering in fancy colors. The bands are slipped while still soft and wet over the neck of the bottle so as to engage the closure; as they dry (two hours or so) they shrink (40%) and make a vapor-tight seal. For liquor bottles on which the revenue stamp has been affixed and must remain visible, the bottle seal is most ingeniously cast with two clear windows (later fitted over the stamp), separated from each other by the dyed or printed portions. Bottle seals consist of short sections of a tubular regenerated cellulose casting, made by extruding viscose upward from an annular nozzle into a coagulating bath. As the newly formed tube rises, it is punctured to relieve the pressure which otherwise develops from gas evolution; the excess bath runs back down. The tube passes over a roller and is guided by other rollers into (and out of) a series of baths which wash and process it. The tubular casting, wound on a spool, is cut mechanically into the proper lengths; these are inspected and packed in tight metal cans, after adding enough solution of a softening agent (glycerin, urea, glucose) to fill the can completely, in order to keep the seal soft and wet until applied.

Sealing caps are the older form of bottle seals and are made on mandrels of various sizes.

The clear tubular casting may be left clear, processed, softened and dried; as such, it forms a sausage casing, much favored by consumers.[12] Making bottle seals is big business; in one plant, for example, 140 million seals are made per month. They are made of cellulose acetate as well as of viscose.

A strong, durable *cellulose sponge* is made from unripened viscose, by incorporating with it Glauber salt crystals of selected sizes and hemp fibers, and packing the well-worked mix into rectangular iron boxes with perforated walls. The boxes are suspended in a salt bath which coagulates the cellulose.[13] Upon heating with steam, the Glauber salt crystals melt and run

[12] The clear tubular regenerated cellulose is famous among chemistry teachers for lecture demonstration of osmosis, and for experimentation in that field. The tubing is obtainable for a nominal sum from the Visking Corporation, 4311 Justine Street, Chicago, Ill.

[13] U. S. Patent 1,909,629, to Hugo Pfannenstiel; earlier patents are 1,142,619 and 1,611,056.

out. The raw sponge, which is dark in color, is washed, centrifuged, bleached, then washed and centrifuged again, and sprayed with a softening solution. The color of the sponge is now the familiar buff. The rectangular sponge blocks, about 8 x 10 x 14 inches, are dried slowly, over a period of four days, in tunnel driers. The dry blocks are viewed in a fluoroscope to detect tramp iron; they are cut into commercial sizes on a band saw. Reverting to the method of manufacture for a moment, a sponge with uniformly fine cellules is made by using fine crystals exclusively; sponges with intermediate cellules are made with medium sizes; sponges with large pores, and generally large in size also, are made with the coarse crystals. Ninety-five pounds of mix becomes $2\frac{1}{2}$ pounds of cellulose sponge.

From the cellulose sponge plant came the bailing sponges with which life rafts carried by seaplanes were equipped, over the war period, and the solar still for making potable water from sea water in extreme emergencies also depended upon cellulose sponges.

Other Patents

U. S. Patent 1,790,990 (Lilienfeld) viscose from cellulose; 1,990,556, on a rubber funnel thread guide; 2,060,964, funnel for spinning rayon; 1,984,853 and 1,986,813, apparatus for spinning rayon; 2,063,180, production of artificial filaments; British Patent 417,920, on artificial products from viscose; U. S. Patents 1,993,816 and 1,990,617, apparatus for making rayon; 2,024,962 and 2,012,723 on rayon manufacture; 2,018,028, 2,010,822, 1,995,732, 2,022,856, on making cellulose acetate; 2,020,247, cellulose acetate composition and plasticizer; 2,010,111, making cellulose esters; 1,990,113, apparatus for manufacture of cellulose esters; 2,279,771, nylon, to insulate and coat electrical wires.

U. S. Patents 1,983,221 and 1,983,795, to William F. Furness (1934) on continuous production of viscose yarn; on same topic, U. S. Patents 2,345,622 and 2,365,096 to A. Mothwurf. U. S. Patent 2,071,250, to Wallace Hume Carothers (1937) on nylon; see article "A review of the nylon patents," begun in January, 1947, in *Rayon Textile Monthly*.

Problems

1. 100 pounds of cotton linters which contain 98 per cent α-cellulose are to be made into viscose. The batch is treated with 15 per cent NaOH to produce the alkali cellulose and the latter is churned with 46 pounds of CS_2. Make an estimate of how much xanthate is formed, using the formula in the text for your composition. By means of 8 per cent caustic, this xanthate is extended to make 1250 pounds of viscose. This is spun, and the yield in the form of filaments in thread form is 88 per cent. What is the weight of rayon obtained?

2. For a daily capacity of 10 tons of product, what volume of viscose with 6 per cent cellulose must be handled, the recovery in this case being taken as 96 per cent? What is the number of tanks you must have ready filled with the viscose for one day's supply, for the production just stated? The tanks are upright cylinders, 6 feet in diameter and 10 feet high. The specific gravity of the viscose is 1.11 at 18° C. (64° F.).

3. Sixteen times the original 125 pounds of sulfite pulp, with a content of 86 per cent α-cellulose, 2 per cent β-cellulose, and 6 per cent hemi-cellulose have been made into a viscose with 6.7 per cent cellulose in solution. This viscose also contains 6 per cent NaOH. In spinning this amount, there will be neutralized in the coagulating bath how much sulfuric acid? And what is the weight of sodium sulfate as Glauber salt which must be removed in order to discard the exact increment of this salt by the neutralization process?

4. Let all of the cellulose in the viscose, as per Problem 3, be made into cellophane, without loss. What will be the weight of the cellophane obtained, allowing for a 17 per cent glycerine content, and a 3.5 per cent residual moisture?

5. A batch of cellulose acetate yarn is manufactured, the cellulose acetate corresponding to 240 pounds of cellulose in suitable form. Using the quantity relations in the text, how much acetate yarn will be obtained, assuming no loss and no waste?

Reading References

"Artificial silk," Dr. Franz Reinthaler, Wien, 1928, translated by F. M. Rowe, Leeds University, New York, D. Van Nostrand Co., 1929.

"Manufacture and properties of regenerated cellulose films," William L. Hyden, *Ind. Eng. Chem.*, 21, 405 (1929).

"Films and fibres derived from cellulose," Dr. Herbert Levinstein, *Trans. Inst. Chem. Eng. (London)*, 8, 24 (1930), with a bibliography.

"Cellulose in industry," H. J. Skinner, *Ind. Eng. Chem.*, 24, 694 (1932).

"Factors during spinning which influence the physical properties of rayon," P. C. Sherer, Jr., and R. E. Hussey, *Ind. Eng. Chem.*, I, 22, 594 (1930); II, 23, 297 (1931).

"Recovery of volatile solvent in a cellulose acetate process, by activated carbon," C. R. Avery and H. Kress, *Chem. Met. Eng.*, 39, 273 (1932).

"Manufacture of chemical cotton (cleaned cotton linters)," W. Donald Munson, *Ind. Eng. Chem.*, 22, 467 (1930).

"The relation of cotton to synthetic fibers," C. E. Mullin, *J. Chem. Ed.*, 7 (2), 1811 (1930).

"The continuous process of manufacturing alkali cellulose," Herbert Fischer, *Rayon Textile Monthly*, 18, 227 (1937).

"Silk culture in south China," Arthur C. Hayes, *Rayon Textile Monthly*, 18, 161 (1937).

"Studies on desulfurization of crude viscose rayon," Philip C. Sherer, *Rayon Textile Monthly*, 18, 33 and 79 (1937).

"Latest foreign developments in the continuous drying of staple rayon," F. K. Howell, *Rayon Textile Monthly*, 18, 35 (1937).

"Development of nylon," an address by E. K. Bolton, medallist, Society of Chemical Industry, *Ind. Eng. Chem.*, 34, 53 (1942).

"Nylon as a textile fiber," G. P. Hoff, *Ind. Eng. Chem.*, 32, 1560 (1940).

"Cellulose acetate rayons," types, properties and uses, Harold Dewitt Smith, *Ind. Eng. Chem.*, 32, 1555 (1940).

"Soybean protein fibers," experimental production, R. A. Boyer, *Ind. Eng. Chem.*, 32, 1549 (1940).

"Vinyon," Frederic Bonnet, *Ind. Eng. Chem.*, 32, 1564 (1940).

"Cellulose sheet swelling, effect of temperature and concentration of sodium hydroxide solution," George A. Richter and Kenneth E. Glidden, *Ind. Eng. Chem.*, 32, 480 (1940).

"Graphic method in rayon manufacture—Control of factory solutions," Joseph H. Koffolt and James R. Withrow, *Ind. Eng. Chem.*, 30, 923 (1938).

"Cordura," W. H. Bradshaw, *News Edition*, A. C. S., 18, 814 (1930).

"Cellulose and cellulose derivatives," Emil Ott, editor, Chapter 8, section F, "Xanthates," by Emil Kline, New York, Interscience Publishers, Inc., 1943.

"Textile fibers, chemical and physical aspects," Jerome Alexander, *Ind. Eng. Chem.*, 31, 630 (1939).

"Textile fibers, their physical, microscopical and chemical properties," fifth edition, Matthews-Mauersberger, New York, John Wiley and Sons, 1947.

"Nylon is big business," *Chem. Industries*, 60, 776 (1947).

The three foods essential to the well-being of man are proteins (meat), fats and carbohydrates; the most palatable form of the latter, cane sugar, is found in nature and needs only to be extracted from the plant. Still another carbohydrate is starch, found in a still greater number of plants, and not usually extracted for food purposes; it is isolated for industrial purposes, and from it, among other things, an artificial food sugar is made.

Chapter 23

Cane Sugar,[1] Beet Sugar, Corn Starch and Glucose

Cane Sugar

Production and Prices

The extraction of sugar from the plant, and the refining of the crude extract, are important industries, for sugar is a favorite and practically universal food. It is estimated that the normal per capita consumption of sugar in the United States is close to two pounds a week. The white crystalline substance which is usually called sugar, is more precisely designated as *sucrose*, a disaccharide. The plants in which it occurs, and which are used as sources, are the sugar cane[2] and the sugar beet; the former grows in tropical countries, the latter in temperate ones. The sugar from the two is identical. The method of extraction from sugar cane is to cut and crush the cane, and to collect the juice which is expressed (Mill House). The juice must be concentrated and crystallized near the plantation, for it contains much water which could not be transported without great shipping expense. Also, inversion of the sugar, with consequent loss of the crystallizable sucrose, becomes pronounced after two or three hours. It is customary therefore to work up the cane juice into a first crystallized sugar (Boiling House). As this first sugar is still colored, it must be refined; this is done in a comparatively few central plants, the refineries, most of which are situated in the temperate countries.

Tropical cane sugar factories are of varying sizes and may produce as much as 160,000 long tons of sugar per annum. They draw their raw material—the cane—from a very wide area. Elaborate rail and road systems are an important part of the organization of the larger modern sugar factories.

[1] In collaboration with Mr. Lionel S. Birkett, General Manager, S. Davson and Co., Ltd., British Guiana, formerly Sugar Technologist, Blairmont Estate, Berbice, British Guiana.

[2] The sugar cane originated in India, and was known to the Greeks and later to the Romans; it spread from there, by the agency of man, in succession, to China, Arabia, Tunis, Morocco, Madeira, the Azores, Cape Verde Islands, Island of St. Thomas, Brazil, Jamaica (1656), San Domingo (1697). Cuba experienced the first blooming of its cane cultivation in 1772, although the introduction had taken place many years before; the cane was brought to Louisiana in 1751; it was also carried to Java at that time.

In many tropical countries, direct-consumption sugars, produced in the sugar factory and called "Yellow Crystal," "Plantation White," and similar names, are often preferred to refined sugar, and are even sold in competition with it in the countries of origin as well as in temperate climates. Contributing to the growth and popularity of direct-consumption sugars has been a change in taste: native people who formerly accepted the raw sugar for their own use, now demand something better. The change is due to the raised standard of living brought about by the war. Another effect of this is that some countries which formerly exported, now not only require their own production, but even import additional amounts. The production of the better sugars at the factory itself has been facilitated by the introduction of vegetable char, which is so cheap that it may be discarded after a single use. However, it is still true that the bulk of the first sugar is shipped to the refineries, there to be made into the familiar snow-white product.

It is well to distinguish three industries, cane-sugar manufacture, cane-sugar refining, and beet-sugar manufacture; the last is so conducted that no refining is necessary. It must be remembered that although the word "manufacture" is used, there really is no manufacture of the sugar, but merely an extraction. From the beet, the sugar is extracted by diffusion.

In many countries, including the United States, a sugar syrup is made from the cane, which serves as sweetening agent. In the north, a small amount of maple sugar and maple syrup is produced.

The relative importance of the various sugar-producing countries in the world is shown in Table 77. In the crop year 1946-47, two-thirds of the world production was from cane, one-third from beets. The production from cane in Cuba, always considerable, rose sharply in this same year; while the production in Java dropped, mainly because of the war, to a record low of 25,000 tons in 1945-46, from 1,678,107 tons in 1940-41. The peak Javan output was 2,942,769 tons in 1928. The production of beet sugar in Germany, 1,400,000 tons for 1946-47, was better than for the previous year, with 750,000 tons; in the earlier war years, the German production was between 2 and 2½ million tons. The Russian production has recovered from the low, 535,000 tons in 1942-43, and reached 2,400,000 tons in 1946-47. The production in France, in Poland, and in other European countries is returning to normal. The production of cane in continental United States is small, but that of its island dependencies (Hawaii and Puerto Rico) is considerable. In the Philippines, the remarkable high of 1940-41 (1,028,354 tons) will probably not be equalled for many years; the 1946-47 production was only 93,000 tons. The record of Brazil is striking: a steady production for years of around 1¼ million tons. Argentina, Mexico and Peru each produced large tonnages. The production of beet sugar in the United States in 1946-47 was 1,330,000 tons, equal to the average yearly figure for the past ten years. In 1943-44, a war year, with sugar badly needed, the production from beets was only 837,776 tons, a record low for the ten years.

The domestic sugar factories and refineries are protected against lower

TABLE 77.—*World sugar production* (in long tons).

CANE SUGAR	1946-1947	1945-46	1944-45	1913-14
America				
Cuba	5,225,000	3,996,391	3,503,788	2,597,732
United States				
Florida	90,000	94,643	60,714	.....
Louisiana	300,000	329,998	329,803	268,337
Puerto Rico	940,000	811,686	860,513	325,021
Hawaiian Islands	760,000	607,000	733,229	550,925
Virgin Islands	5,000	4,332	5,000	5,800
Dominican Republic	456,000	451,671	363,000	105,778
Haiti	45,000	39,121	44,880	.....
British West Indies	480,210	465,341	385,220	136,257
French West Indies	95,000	75,000	36,044	66,298
Mexico	400,000	423,600	371,600	127,944
Central America	120,000	111,500	112,349	22,000
Argentine	600,000	449,147	459,354	280,319
Brazil	1,320,000	1,269,420	1,197,853	158,038
Peru	395,000	390,000	431,520	228,054
Other South America	312,000	314,105	303,693	128,594
Total in America	11,543,210	9,832,953	9,199,151	5,001,097
Asia				
British India (Gur)	3,800,000	3,652,960	3,713,480	
(White Sugar)	1,000,000	1,035,000	1,059,830	2,291,500
Java	250,000	25,000	84,245	1,272,417
Japan	150,000	166,785	950,000	157,050
Philippines	93,000	12,837	67,000	232,761
Total in Asia	5,293,000	4,892,582	5,874,555	3,953,728
Africa				
Egypt, Mauritius, Reunion, Natal, Mozambique	1,122,000	982,110	1,062,428	480,956
Australia and Polynesia				
Australia	545,000	665,507	669,898	266,267
Fiji Island	115,000	64,992	63,010	92,112
Europe: Spain	12,000	12,000	9,458	7,376
Total Cane Sugar	18,630,210	16,450,144	16,878,500	9,801,536

world producing costs in two ways: by a protective tariff [3] and a quota for each producing country expressed as a percentage of the requirements of the

[3] The tariff for 75° sugar was 1.7125 cents per pound, with 0.0375 cent more for each additional degree, in the U. S. Tariff Act of June 18, 1930. Cuban sugar is 96°, hence should pay 2.50 cents per pound; a 20 per cent preferential is applied, however, so it paid 2 cents. In the U. S. Tariff known as the Flexible Tariff, of June 8, 1934, the duty was reduced; it has been changed by supplementary agreements several times since then, both ways. The rate now in force is in the agreement of January 5, 1942, which provides, for Cuban sugar, a duty of 0.51375 cent per pound of 75° sugar, 0.01125 cent additional for each degree, making 0.75 cent for 96° sugar. Since July 29, 1942, other foreign countries pay 0.9375 cent for the 96° grade. Cuba therefore still has a 20 per cent preference. The degree of sugar is obtained by reading the rotation of a beam of polarized light. The magnitude of the rotation is proportional to the amount of cane sugar present. In "direct polarization," the instrument is so arranged, and the amounts of sample and solvents are so chosen, that the degree read is also the percentage of sucrose, without any further calculation.

TABLE 77.—*World sugar production* (in long tons)—(*Continued*).

BEET SUGAR	1946-1947	1945-46	1944-45	1913-14
America				
United States	1,330,000	1,064,261	881,106	655,298
Canada	85,000	73,237	73,793	11,675
Total in America	1,415,000	1,137,498	954,899	
Europe				
Germany	1,400,000	750,000	2,190,205	2,617,937
Czechoslovakia	575,000	457,472	567,324	B
Russia and Ukraine	2,400,000	1,500,000	850,000	1,687,799
France	675,000	456,500	323,400	717,400
Poland	450,000	191,827	300,000	C
Holland	210,000	60,000	40,700	229,257
Italy	275,000	23,000	70,000	304,977
Spain	175,000	118,000	122,542	169,355
Belgium	225,000	140,518	194,898	229,049
Hungary	75,000	7,319	124,789	
Roumania	50,000	25,807	34,322	34,758
Gt. Britain and Eire	630,000	614,912	485,325	
Denmark	200,000	183,712	176,439	145,700
Sweden	300,000	294,300	301,139	137,082
Austria	.....	.....	.....	1,682,678
Other Countries	307,000	249,241	215,500	11,977
Total in Europe	7,947,000	5,072,608	5,996,583	7,967,969
Total Beet Sugar	9,362,000	6,210,106	6,951,482	8,634,942
Grand Total				
Cane and Beet Sugar	27,992,000	22,660,250	23,829,982	18,436,478

B, included in Austria; C, included in Russia.
From Manual of Sugar Companies, 1946, Farr and Co., New York 5, N. Y.

continental United States[4] (Sugar Act of 1937). The Sugar Act of 1948 provides fixed quotas for domestic sugar-producing areas and for the Philippines, and proration of the balance of consumption estimate to other countries; it will remain in effect for five years.

During the war, a ceiling price for granulated refined sugar within the United States was set at just under 5 cents a pound by the Government office in Washington; the ceiling for raw sugar, more specifically Cuban raws, duty paid at New York, at the same period was 3.75 cents a pound. The basic minimum price for the 1947 crop of Cuban raw sugar was set at 4.925 cents per pound f.a.s. Cuba. The ceiling price at wholesale for refined cane sugar in September, 1947, was 8.4 cents; for beet sugar, 8.3 cents per pound.

In the evaluation of sugar, the fact is utilized that sucrose dissolved in water rotates the plane of polarized light to the right; the invert sugar which is formed from sucrose by the action of enzymes or of acids rotates the plane of polarized light to the left. Other impurities have little effect

[4] Domestic beet sugar producing areas, 23.19 per cent; domestic cane from the mainland, 6.29 per cent; Hawaii, 14.04 per cent; Puerto Rico, 11.94 per cent; Virgin Islands, 0.13 per cent. The foreign producers: Cuba, 28.60 per cent; Philippines, 15.41 per cent; others, 0.40 per cent. The sugar quotas were suspended on April 12, 1942, and remained suspended until 1948.

on the polarized beam. In a pure sucrose solution, the rotation of the light beam to the right is a measure of the sucrose content. It is arbitrarily assumed that the same holds true for a solution of raw sugar.

The instruments used are the polarimeter,[5] which reads in circular degrees, or the saccharimeter, which permits readings on an horizontal scale running from 0 to 100. In the saccharimeter, 0 represents pure water and 100 a solution of pure sucrose in a definite concentration (26.0 grams in 100 milliliters, read in a 2-decimeter tube). The readings are called degrees, and raw sugar usually reads 96° and a fraction on this instrument.

The reaction for sugar inversion with the degrees of rotation for the pure substances in each case, and the direction of rotation (+ for right or dextro, − for left or levo) is:

$$\underset{\substack{\textit{sucrose}\\ +66.56^\circ}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\substack{\textit{d-glucose}\\ +52.8^\circ}}{C_6H_{12}O_6} + \underset{\substack{\textit{l-fructose},\\ -92.8^\circ}}{C_6H_{12}O_6}, \quad \text{hence} \quad \frac{+52.8 - 92.8}{2} = -20.0^\circ.$$

The sum of the rotation of the two mono-saccharides, on the right of the equality sign, is a negative rotation; hence there is an inversion of the sign.[6] Glucose and fructose are sometimes called reducing sugars, because they reduce Fehling's or Benedict's solution, whereas sucrose does not.

Sugar from the Cane

The sugar cane is a large perennial grass which attains a length of 10 to 24 feet at maturity. There are a number of species and numerous varieties. Sugar cane is propagated by cuttings, each cutting consisting of portions of the cane plant having two or more buds. The buds develop into cane plants from which several other shoots arise from below the soil level to form a clump of stalks (stool). From 12 to 20 months are required for plant crops (new plants) and about 12 months for ratoons, that is, cane stalks arising from stools which have been reaped previously. Fields are replanted after 2 to 5 reapings have been obtained from the original cuttings. The cane stalk is round, 1 to 3 inches in diameter, and is covered with a hard rind, light brown, or green, yellowish green, or purple in color, depending on variety. The stalk is made up of a series of joints or internodes separated by nodes (not unlike bamboo). The rind and the nodes are of a woody nature, while the internode is made up of soft pith. The internode contains the greater part of the juice. In harvesting, the canes are cut at ground level and the leaves and tops of the stalks are removed. The sucrose content of the ripened cane varies between 10 and 15 per cent of the total weight, with 13 per cent about average.

Juice Extraction, Mill House. The cane is first cut into short lengths by rapidly revolving knives, and then passed to a milling train which may consist, for example, of a two-roll crusher followed by four three-roll mills, in all 14 rollers, where the juice is squeezed out by pressure (Figure 188). The rolls in the three-roll mills are under a pressure of 75 to 80 tons per foot

[5] The polarimeter in the form of the polariscope, a half-shadow instrument, is due to the invention of Antoine Laurent. There are now many forms and variations of the instrument.

[6] The name "invert sugar" arises from the change in the sign of rotation.

FIGURE 188.—A sugar cane mill seen from the top. The knifed cane is fed into the crushing train down the chute at right, and into a three roll crusher, of which the top roll is visible. The crushed bagasse, now extremely fine in texture, next passes into the three roll mill, of which again the top roll is visible. A screw conveyor (center) brings the deposited bagacillo from the juice strainer back into the mill. (Courtesy of The Squier Corporation, Buffalo 4, N. Y.)

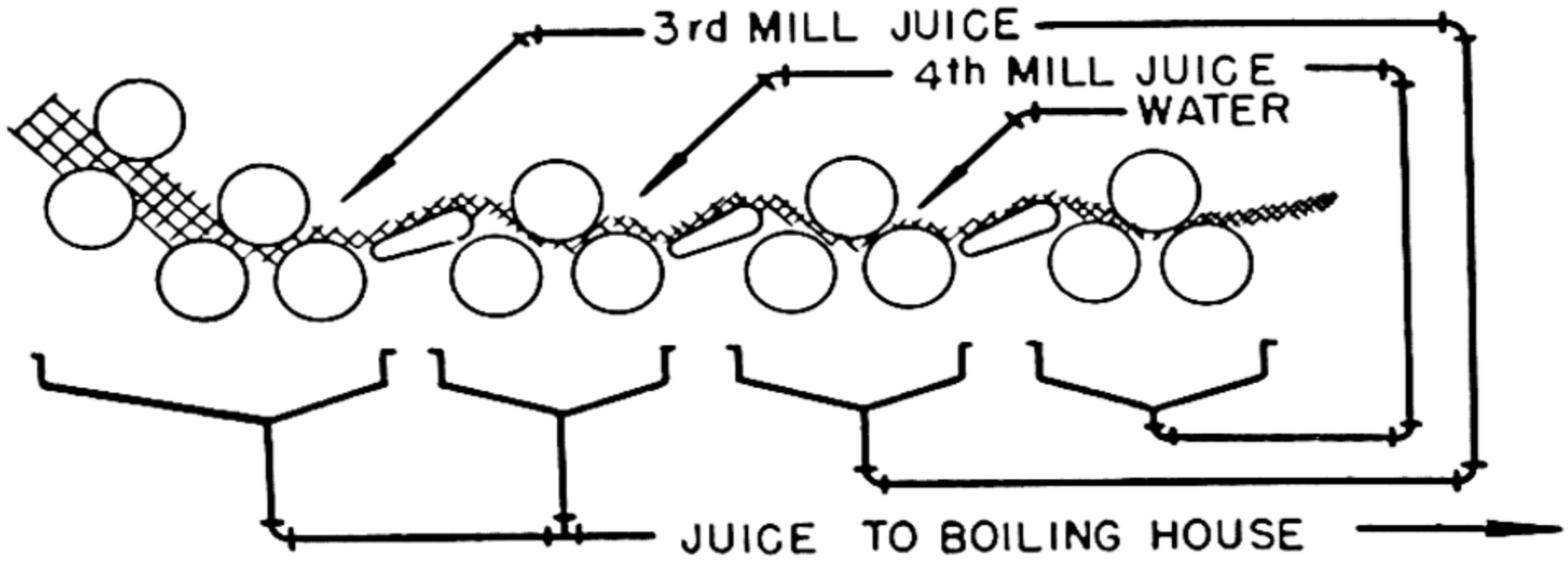


FIGURE 189.—A milling train consisting of a crusher and four three-roll mills, grinding with the application of water: compound imbibition.

of roll length, and the length ranges from 2½ to 7 feet; the crushing varies with the length of the roll, from 500 tons for the small length to 5000 tons per 24 hours for the larger mills. In the process of milling, water is applied to the crushed cane and the lean (dilute) juices are returned to the mills. In a 14-roller milling train, water is applied to the cane at the third mill, and its juice is fed to the first mill; the juice from the fourth mill is fed to the second mill. The method is known as compound imbibition. The approxi-

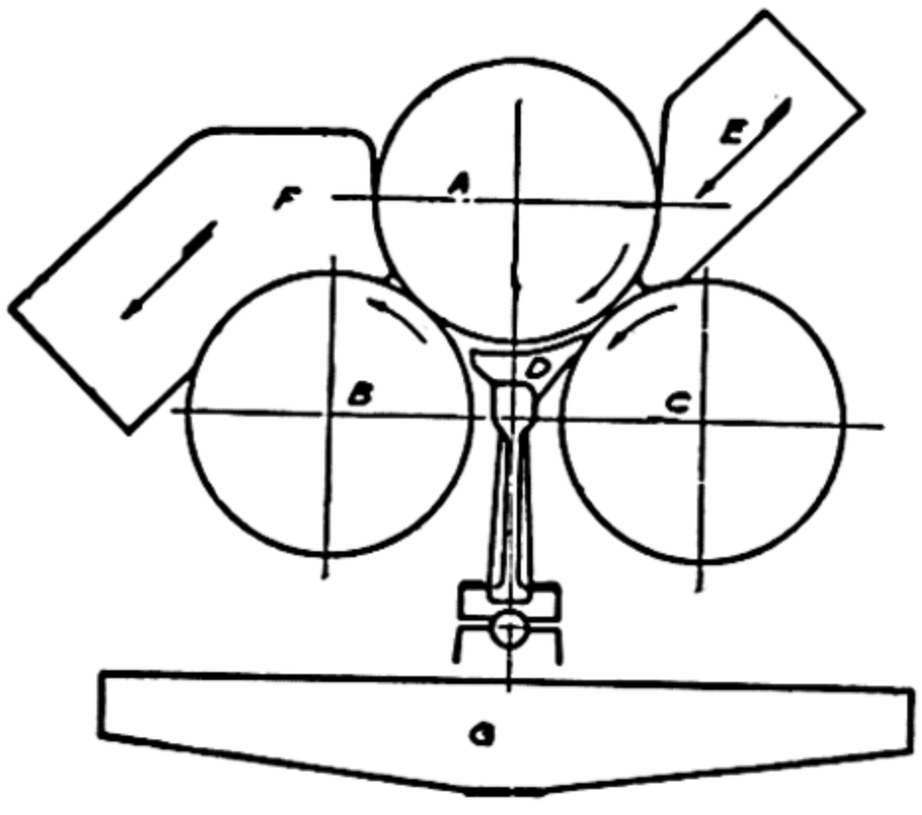


FIGURE 190.—A cane mill with its three crushing rolls, and with typical turn-plate arrangement. *A*, top-roller; *B*, bagasse roller; *C*, feed roller; *D*, trash plate; *E*, feed of cane; *F*, discharge of crushed cane; *G*, juice-collecting trough. A hydraulic piston maintains pressure on *A*, while *B* and *C* are fixed; the rolls are under a pressure of 75 to 80 tons per foot of roll width.

mate percentage of the sucrose in the cane extracted by each unit of the milling train is about as follows:

Crusher	1st Mill	2nd Mill	3rd Mill	4th Mill	Total
70.0	12.5	7.0	4.5	2.0	96.0

The composition of the juice varies with soil and climatic conditions, cane variety and degree of maturity, within the limits indicated below:

Water	Sucrose	Reducing sugars	Other organic Compounds	Ash	pH
78-86%	10-20%	0.5-2.5%	0.5-1.0%	0.3-0.7%	5.1-5.7

As shown by the pH value, the juice is acid; it is strained through a perforated metal sheet and sent to the Boiling House where it is clarified and concentrated by boiling. The bagasse from the last mill of a train contains from 52 to 58 per cent of solid matter, mainly cane fiber, and the balance is water. Its main use is as a fuel for raising the steam required by the factory; large amounts serve to make "Celotex" for sheathing frame houses, for wallboard, and for insulation.

Clarification of the Juice; Defecation. The juice from the strainer is clouded by small amounts of suspended and colloidal matter, and hence must be clarified. For the manufacture of raw cane sugar which is to be refined elsewhere later, simple lime defecation is practiced. Milk of lime is added to the juice in amounts sufficient to raise the pH to 7.6 or 7.8. The limed juice is pumped through high-velocity juice heaters (heat exchangers, steam versus juice); insoluble calcium phosphates, sulfates and other salts form which adsorb and entrain in their precipitation a large proportion of colloidal impurities (waxes, pectins and pentosans), the flocculation of which is

also promoted by the alkaline reaction. In addition, insoluble proteinates are formed, and the elimination of proteins is fairly complete. Should the juice contain less than 0.03 gram of P_2O_5 per 100 milliliters, enough phosphoric acid or superphosphate is added to bring the amount up to that figure. Precipitation may take place in settling tanks, or in continuous shelf clarifiers such as the Graver[7] or the Dorr,[8] from which the juice emerges in crystal clear condition, and is pumped to the evaporators. The sediment from the settlers is filtered, the filtrate returned to the subsiders, and the solids to the fields as fertilizer.

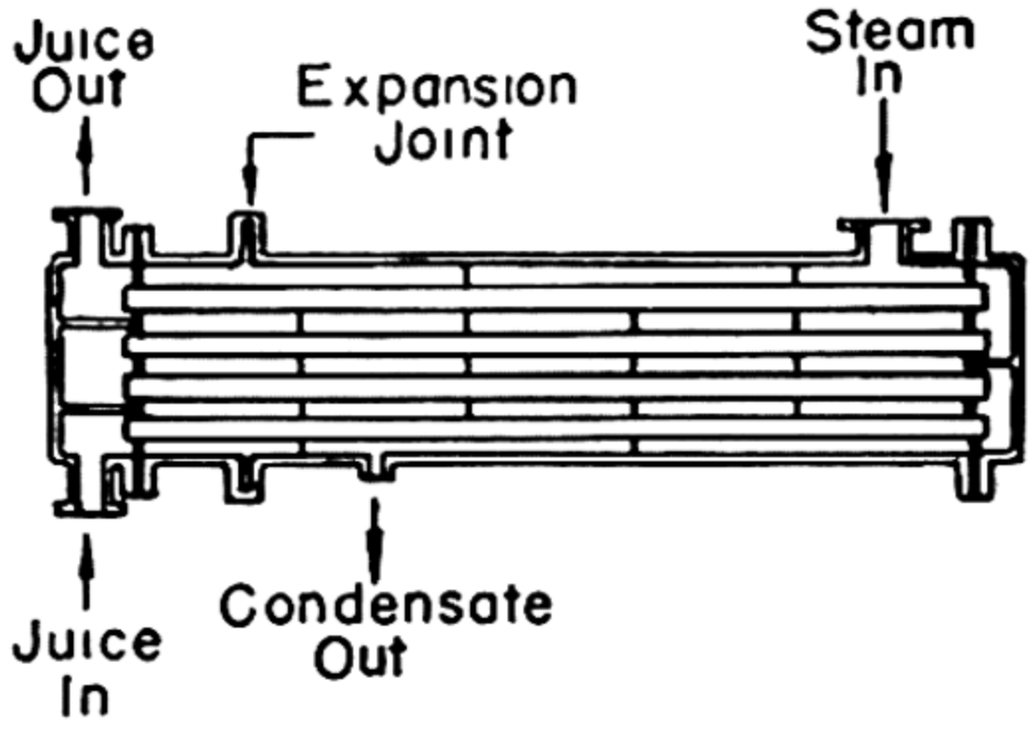


FIGURE 191.—A juice heater.

First Evaporation to Syrup. The clear juice from the settlers passes to a triple- or quadruple-effect evaporator, where it is concentrated to a clear, brilliant, pale-yellow syrup (about 30° Bé.). The operation is continuous. The evaporator functions under a vacuum which differs from effect to effect.[9] Examination of the diagrammatic flow sheet (Fig. 192) will reveal that part of the "vapor" raised in the pre-evaporator is drawn off to the juice heaters, while another part may be used to operate a vacuum pan (see later). The remaining "vapor" enters the calandria of the second effect evaporator. About 70 to 75 per cent of the water present in the clarified juice is removed in the evaporators, the resulting syrup having a content of from 55 to 64 per cent of soluble solids. The syrup is pumped to storage tanks situated on the pan floor.

Crystallization of Sucrose. The syrup is concentrated further in a single-effect vacuum pan (the strike pan), in which vacuum and steam may be regulated as the operator deems necessary. In the triple- or quadruple-effect evaporator for the first evaporation, exhaust steam (5 to 12 lbs per sq inch) is employed; in the vacuum pans equipped with large copper heating coils, boiler steam is used; while in the vacuum pans with calandrias low-pressure steam may also be used. All vacuum pans have batch operation. By suitably arranging the heating surface and the shape of the pan, constant circula-

[7] Described and illustrated in "Chemical Machinery" (pages 253-256) by Emil R. Riegel, New York, Reinhold Publishing Corporation, 1944.
[8] *Ibid.*, p. 256.
[9] See Chapter 43 in this volume; or Chapter 15, on Evaporators, in "Chemical Machinery," by Emil R. Riegel, New York, Reinhold Publishing Corp., 1944.

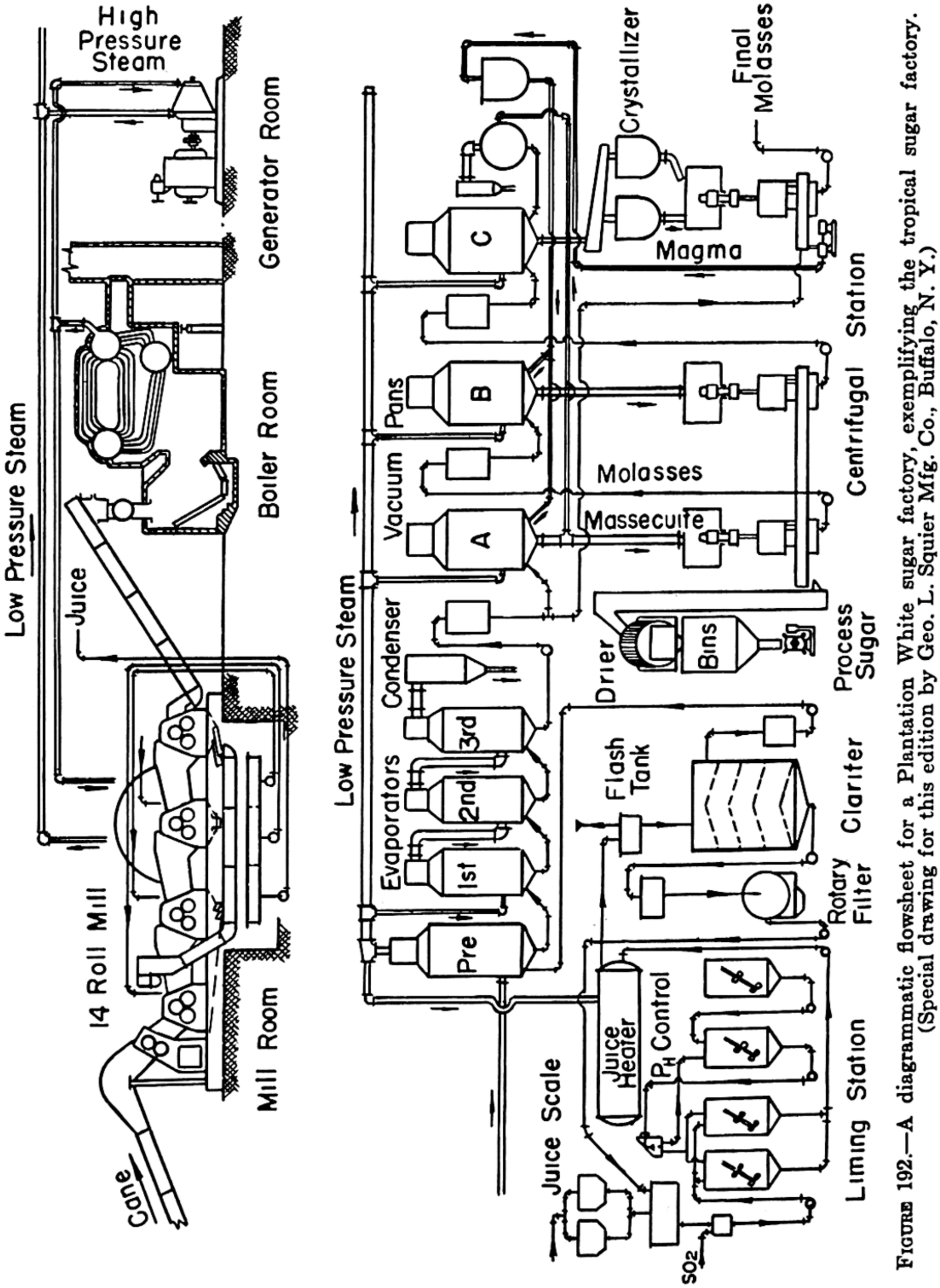


FIGURE 192.—A diagrammatic flowsheet for a Plantation White sugar factory, exemplifying the tropical sugar factory. (Special drawing for this edition by Geo. L. Squier Mfg. Co., Buffalo, N. Y.)

tion of the mass within the pan is assured; in recently erected vacuum pans, a mechanical circulator is provided.

The syrup is evaporated until a blob on a glass plate examined by lamplight glistens because numerous small crystals or nuclei have been formed; this point is called the graining point. More syrup is then added, in small portions, and sugar, forced out of solution by evaporation, deposits on these nuclei, causing them to grow. This is continued until the desired growth has been attained and until the pan is full; the semi-solid mass in the pan is

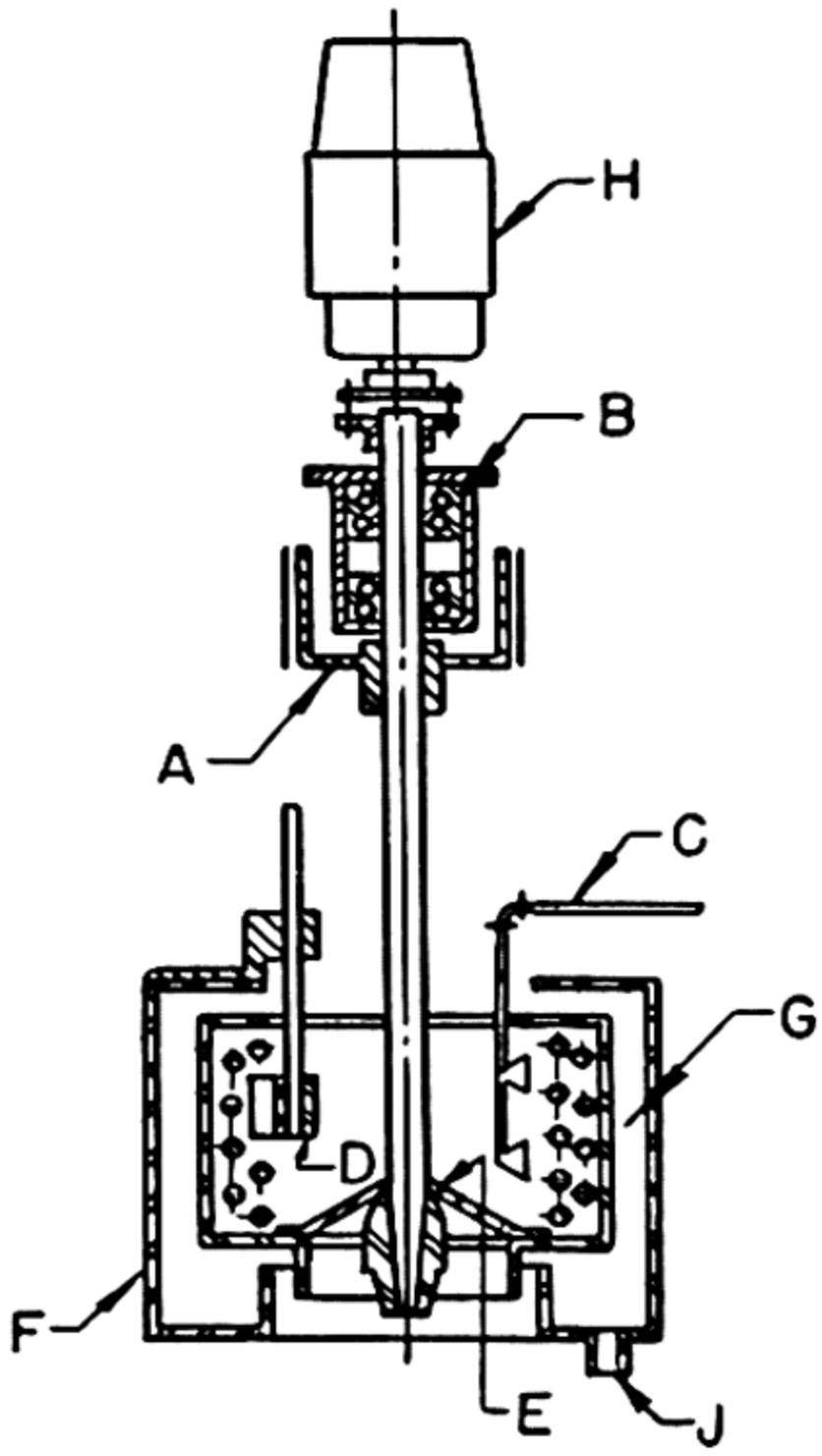


FIGURE 193.—A centrifugal for the separation of sucrose crystals from the mother liquor. *A*, brake drum; *B*, ball bearings; *C*, wash water; *D*, plow for discharging the dry crystals; *E*, discharge gate; *F*, curb or casing or monitor; *G*, perforated centrifugal basket. Not shown, the fine-screen lining on inside of basket.

called "massecuite" and contains a total of about 82 per cent of sucrose in the case of massecuites produced from syrup ("A" massecuites). The "A" massecuites will yield about 54 per cent of their weight as crystals; the others ("B" and "C" massecuites) less. The control of the number of nuclei is very important; if they are too few, there will be more sugar ready to deposit than surface to receive it, and later there will be a new crop of nuclei which will grow poorly (false grain). If too many nuclei are present, the crystals will be too small, and the separation in the centrifuge will be slow and imperfect; when this happens, only part of the pan is dumped, and on the rest as a "footing," more syrup is introduced; thus with the proper number of nuclei, the regular crop of crystals is developed.

When a vacuum pan which has been working on syrup from the evaporators is full and ready, it discharges its massecuite while hot into receivers, from which it is fed to centrifugal baskets.[10] The centrifugal ma-

[10] See Chapter 14, "Chemical Machinery," footnote 7.

chine has a vertical shaft, and its perforated cylindrical basket is lined with a closely woven metal mesh through which the molasses can pass but the crystals cannot. When the basket is set in motion, the centrifugal force drives the massecuite against the wall of the centrifugal, and the molasses goes through the crystals and the mesh into the outer casing. After the molasses has drained away, the centrifugal is stopped and the sugar discharged through a valve at the base of the centrifugal basket into a conveyor placed beneath it.

The sugars so obtained possess a film of molasses which gives them a greyish brown color. Water added in the form of a spray to the surface of the sugar in the centrifugal while revolving at high speed dilutes and washes off this layer of molasses and yields a whiter sugar.

A single crystallization does not permit all the recoverable sucrose from cane syrups to crystallize; accordingly, after obtaining a crop of crystals from the syrup massecuites, it is necessary to reboil the molasses obtained therefrom to obtain a further yield of sucrose crystals from it. Usually two or three reboilings of molasses are necessary to recover the maximum of crystallizable sucrose. Sugar from the "C" massecuite is not usually one of the products of a cane-sugar factory, as this grade of sugar is used as nuclei for "A" and "B" massecuites, which are thus converted into a product of higher grade and value; "C" sugar also serves to reduce the amount of "graining" which would otherwise be necessary. The crystals obtained from the "A" and "B" massecuites are mixed and bagged together as raw sugar, which constitutes the main product of a cane-sugar factory.

The massecuites yielding exhausted molasses contain considerably higher proportions of non-sucrose components relative to sucrose than did the original cane syrups. Consequently, these low-grade massecuites are usually extremely viscous. Since the mother liquor obtained from them will finally become molasses, it is necessary to insure that as high a yield of sucrose as possible is obtained from them. When discharged from the pan massecuites are at a temperature of from 145° to 155° F. (63° to 68° C.), and since the solubility of sucrose decreases with temperature, further crystallization of sucrose may be obtained by allowing these massecuites to cool to room temperature. This cooling takes place at a slow rate in U-shaped or cylindrical vessels having hollow, water-cooled stirring arms which maintain a gentle movement in the massecuite. This movement induces the sucrose coming out of solution to be deposited on crystals already present instead of forming "false grain." The process is called crystallization-in-motion, and the vessels the "crystallizers."

The molasses obtained from the "C" massecuite is the final or exhausted molasses and is also known as blackstrap.

Approximate data for syrups and molasses massecuites and the molasses obtained therefrom vary considerably; the figures given below should be regarded as only indicative of general practice. "Apparent Purity" expresses the sucrose determined by simple polarization as a percentage of total solids as indicated by measurement of specific gravity.

TABLE 78.

Type of Massecuite	Brix* Solids	Massecuite Polarization per cent	Apparent Purity	Yield of sugar per cent	Molasses Apparent Purity
"A" (syrup)	93.0	76.26	82.0	52-54	62.0
"B" (magma footing +syrup+"A" molasses)	94.0	65.80	70.0	40-42	48.0
"C" (syrup+"B" molasses)	96.0	53.76	56.0	35-38	28-30

* See footnote 11.

The various products of the tropical cane-sugar factory are therefore the 96° crystal sugar (raw sugar), direct-consumption sugars (to be discussed later), occasionally the "C" sugar (molasses sugar) of lower grade, blackstrap molasses, bagasse, and filter cake (which is used as a fertilizer).

Direct-consumption Sugars: The manufacture of direct-consumption sugars is similar to that of raw sugar except that special care is taken in the clarification process, and that reducing agents are added to the syrup or massecuites. Improved clarification is obtained by the addition of sulfur dioxide or carbon dioxide at the liming stage. The precipitated calcium sulfite and calcium carbonate remove greater quantities of non-sugars than simple lime defecation. In the manufacture of Yellow Crystal sugar an acid juice sulfitation process is practiced; by the action of the calcium bisulfite present in such juices, color formation during concentration in the evaporators and pans is greatly reduced. Furthermore, small quantities of stannous chloride are added to the syrups; in some factories, organic dyes are dissolved in the water used for washing the crystals in the centrifugals. When manufacturing Plantation White, sodium hydrosulfite may be used at the pans.

Cane Sugar Refining

The raw cane sugar purchased by the refinery in the temperate climate countries contains as a rule 96 to 97½ per cent of sucrose. The task of the refiner is basically a recrystallization, preceded by a treatment to remove color. The analysis of a typical raw cane sugar would be approximately as follows:

Sucrose	Reducing sugars	Other organic compounds	Ash	Water
97.50%	0.86%	0.46%	0.43%	0.75%

At the refinery, the raw sugar is mixed with a mother liquor from a previous batch, which removes a large part of the color, but leaves the crystals for the most part undissolved. The mass is centrifuged, the crystals washed while in the basket, then removed and dissolved in hot water to form a syrup. A small amount of lime is added and steam blown in, after which the syrup is passed through bone char held in tall cylinders 20 feet high and 3 feet in diameter. The function of the bone char is to adsorb the remaining color, and to act as a filter. The liquor then goes to the "strike pan" and is there concentrated to massecuite, as was described under raw sugar; the massecuite is centrifuged, and the crystals dried in a rotary drier, to produce granulated sugar. Or, the white massecuite may be solidified to a loaf, which may be

cut into regular cubes or into flat pieces (Domino sugar). There are many other modifications which lead to special forms.

The bone char in the filters is used until it no longer bleaches because its pores have become clogged with impurities. In order to reclaim it, water is turned into the cylinders to remove most of the adhering sugar; then the char is dumped and revivified by heating it in the absence of air to red heat. It may then be used over again. After a number of such treatments, it disintegrates, and is disposed of to the fertilizer trade for its phosphate content.

The mother liquor at the centrifugals is collected and used again; even after several uses the mother liquors are still rather pure, although colored pale brown. They are then usually made into syrups, either unmixed, or blended with maple syrup.

Under favorable circumstances, a raw sugar may be refined by mere mixing with a mother syrup, centrifuging, washing the crystals with sugar solution and finally with steam, to produce a nearly white product.

New methods, some of them especially adapted to refining in the tropics, have been introduced. The activated carbon process has been most successful: raw sugar is washed in the centrifugal to give a sugar polarizing 98.5 to 99°. It is then made into a syrup to which monocalcic phosphate, slaked lime and kieselguhr are added and the mixture is then heated and filtered. The filtrate with pH 6.0 to 6.4 is mixed with a small percentage of vegetable carbon ("Suchar," "Norit," "Darco") and filtered again, this time on precoated filters. The resulting clear and colorless syrup is then crystallized in the usual manner, and dried. The vegetable char is used once, or at most a few times, and is then discarded.

Another very successful, and very different method employs "*Sucroblanc*," the procedure being as follows: The raw sugar is first "washed," by making it into a mash with green liquor or other sugar liquor, and purging it in centrifuges. The resulting "raffinated sugar" is dissolved in hot water to 60 or 65° Brix,[11] and 0.1 to 0.3 per cent of the reagent "Sucroblanc"[12] stirred in at room temperature or slightly higher. The reagent contains high-test calcium hypochlorite such as "Perchloron," and, in addition, calcium superphosphate, lime and "Filtercel." There is a slight evolution of gas (oxygen) which causes the colloidal impurities to rise to the top of the solution; the clear, decolorized sugar solution may be drawn off from the bottom. Thus two steps in the older process (defecation and bleaching) are here combined into one. The clear sugar solution goes to the evaporator and strike pan to make crystal sugar.

Recently there have been placed in use several variations of *ion-exchange processes for refining sugar*; usually the procedure includes passing the unheated syrups to be treated to a solid bowl centrifugal, then through filters of positively and negatively charged beads successively.[13] The beads when

[11] The Brix scale is a density scale for sugar (sucrose) solutions. The degrees Brix are numerically equal to the percentage of sucrose in the solution. The term "Brix solids" refers to the solid content as determined by the Brix hydrometer.

[12] U. S. Patents 1,989,156 and 2,091,690. Compare also "Modern Sugar Refining," *Chem. Met. Eng.*, **47**, 119 (1942).

[13] U. S. Patent 2,388,194 (Oct. 30, 1945) for removing ions from raw sugar juices; 2,413,791 (1947); 2,413,844.

inactivated are washed and reionized. Exhausted molasses which formerly was inedible, becomes palatable and mild when purified with ionized materials. Moreover, the yield of sugar per ton of cane is higher.

Sugar from the Sugar Beet

Within the United States, Michigan, Utah, Colorado, and coastal California are the main producers of beet sugar.[14] Thanks to the efforts of European scientists a strain of beets has been developed which produces beets containing as high as 18 per cent sucrose, rivaling the sugar cane.

At harvest time, the beet root, free from the leaves, is carted to the sugar house, washed free from dirt, and cut into V-shaped slices about one-quarter inch thick; these are the "cosettes" or noodles. They are fed to a number of diffusion vessels, so arranged that the noodles may be delivered to any one of the 20 or more vessels from one overhead spout. The extraction is by hot water, in contact with the slices, on the countercurrent principle. Hot water enters the diffuser whose charge is nearly exhausted; sugar diffuses from the cells of the beet into the water; the solution travels to the next diffuser, whose slices are richer. The solution leaving the last diffuser was in contact with a fresh charge. In this way the solution is strengthened until it contains about 12 per cent sucrose, forming a dark solution. The exhausted noodles are washed out of the tank to a receiving box where they dry and are carted away to farms, to serve as cattle food.

The warm diffusion juice is agitated with 2 to 3 per cent of lime for two hours, after which carbon dioxide is passed in to saturation. The precipitate which forms carries down nearly all impurities; the juice is filter-pressed, and in some plants is treated with lime followed by carbon dioxide a second time, and even a third time. The filtrate obtained is pale yellow; most of this color is removed by sulfur dioxide, which also decomposes some salts of calcium with organic acids, precipitating calcium sulfite. As a rule, the sulfur dioxide treatment follows the first lime treatment. The filtered solution ready for the evaporators is purer than the corresponding solution from the sugar cane. The concentration is performed in double- or triple-effect evaporators, to a clear syrup, as for cane juice, and this is followed by graining in the vacuum pan. The crystals separated by centrifuging are washed in the basket, and after drying, are ready for the market. The mother syrup is concentrated again, giving crystals which are re-worked, and a mother liquor, the molasses. As much sugar is crystallized from the molasses as possible; the remaining sugar is recovered by a chemical process, to give finally crystal sugar for the greater part. In other factories, the molasses is sold as such for consumption. Beet sugar molasses is rarely used for making industrial alcohol.

The sugar in the molasses may be recovered by diluting to about 7 per cent sugar, cooling to 12° C. (53.6° F.), and adding pulverized lime from a Raymond type mill[15] while agitating violently; tricalcium saccharate precipitates. It is filter-pressed and washed and serves instead of lime in the

[14] For other beet sugar producing countries, see Table 77 in this chapter.
[15] Chapter 44.

purification of the warm diffusion juice (Steffen process). When this process is used, the total recovery of sucrose in the beet is 85 to 88 per cent.

There is still sugar left in the mother liquor from the Steffen process; it may be recovered by means of the barium saccharate process, successfully operated by a large American beet sugar company. Barium hydroxide is added to the discarded molasses; the sugar precipitates as monobarium saccharate, which is filtered, and decomposed by means of carbon dioxide. There are formed barium carbonate, and a solution of sugar which is worked up as usual. The barium carbonate is put through a cyclic process, for the regeneration of barium hydroxide. The carbonate is mixed with sand, or monobarium silicate from a previous run, and furnaced to form dibarium silicate. This latter is suspended in hot water, giving a solution of barium hydroxide and monobarium silicate. The sugar produced by this process is of the highest purity.

By alkaline hydrolysis of the concentrated Steffens waste there is recovered the monosodium salt of l-glutamic acid.[16]

Monosodium-l-glutamate is a flavor-accentuating agent.

$$HOOC\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH$$

l-glutamic acid

a solid

Other forms of sugar are sorghum or sorgho syrup (Alabama), maple syrup (Vermont and New York), and honey, at one time of great importance; to these natural sugars, manufactured glucose, described in the latter part of this chapter, must be added. Glucose from starch is presented in this chapter, and "sugar by the hydrolysis of wood cellulose" is part of Chapter 16.

"Celotex"

Instead of burning bagasse under boilers, it may be made into a building board called "Celotex." The bagasse is freed from gums and waxes and the resulting pulp made into sheets one-quarter inch thick, very much as cardboard is made. After drying, the resulting board is suitable for sheathing buildings, either as outside covering or under clapboards and shingles. It is stronger than wood, and has a high insulating value.

Starch

Starch, like sugar, occurs as such in the plant and requires only extraction. Corn is 65 per cent starch; wheat, rye, and rice contain a high percentage of starch; potatoes contain 15 per cent. If a raw potato is grated, and the gratings gently agitated in a tumbler of water, a cloudy liquid forms which, strained from the pulp, deposits a white powder in a short time; this powder is the starch. The process of extraction in every case is essentially as given, but with a great variation of details. Starch is a food; heated with water it partly dissolves, and the solution has adhesive properties, which leads to its use as a size. Hydrolyzed, the large starch molecule $(C_6H_{10}O_5)_n$ gives dextrin or British gum, with a somewhat

[16] "Manufacture of monosodium glutamate," Paul D. V. Manning, R. W. Shafor, and F. H. Catterson, *Chem. Eng. Progress*, **44**, 491 (1948).

smaller molecule; maltose, the disaccharide, on continued hydrolysis; and finally, *d*-glucose, the monosaccharide, discussed under sugar. To some extent, all these products are formed at the same time; on lengthening the process, more dextrin passes into the lower forms; with the longest treatment, all the starch passes into *d*-glucose.[17] The hydrolysis is hastened by the use of dilute mineral acids, and these are therefore used for the production of commercial glucose, the syrup, from starch; for this manufacture, starch extracted from the plant becomes a raw material.

Starch from Corn (Maize) and Corn Oil. In the United States, starch is made almost exclusively from corn.[18] The corn is steeped in water which contains a small amount of sulfurous acid (H_2SO_3), chiefly as a germicide; the softened grain is shredded in squirrel-cage disintegrators,[19] and next suspended in water, with agitation. The corn seed, or germ, floats easily and is run off with a gentle flow of water from the surface of the tank; the hull, starch, and gluten remain in the water and are run off at a lower take-off.

The germs are rich in oil; they are collected, dried, and pressed for the oil in a way very similar to the pressing of flaxseed for linseed oil[20]; the product is corn oil. The press cake serves as a cattle food.

The suspension containing the starch is screened through bolting cloth stretched on a frame of wood to form a cylinder, which slowly revolves about its long axis; starch and gluten pass through, the hull is retained. The starch suspension is next passed through a long shallow trough slightly inclined at the far end; the starch grains settle in the trough, while the gluten floats off. The separation is not perfect; even after repeating it the gluten still contains a large percentage of starch. The gluten is made into gluten meal (filter press) for special breads.

The starch in the troughs or runways is shoveled onto small cars, washed again for certain grades, settled and dried at a low temperature.[21]

Glucose

Starch is converted into commercial glucose by hydrolysis, using a 0.5 per cent sulfuric acid solution. In Europe, hydrochloric acid is generally used. The starch is suspended in much water, the acid added in a preliminary, open converter, and the whole heated with steam; after an hour, it is transferred to the closed converter, of copper, and heated further by direct steam under a pressure of 50 pounds; the time in the second converter varies from 10 to 20 minutes. The discharged product is neutralized with soda ash; impurities

[17] The old name for dextro-glucose, namely dextrose, has become irrational since the synthesis of levo-glucose has been achieved, and should therefore be abandoned.

[18] In 1914, 97.4 per cent of the starch made was from corn, 1.6 from potatoes, 1 from wheat. In Germany, potatoes are the usual source (U. S. Tariff Commission, *Tariff Information Survey* G 14, 1921, p. 14); in 1929, 93 per cent of the starch made was corn starch (U. S.), and in 1935, 90.7 per cent.

[19] Chapter 44.

[20] Chapter 29.

[21] The long shallow troughs are also called starch tables. In one plant at least, the tables have been replaced by special centrifugals (Merco); in four other plants, such replacements are planned. The tables require too much space. See "Centrifugals replace tables for separation of starch and gluten," R. L. Taylor, *Chem. Ind.*, 62, 54 (1948).

separate in the neutral solution, are filtered, and the clear filtrate is passed through bone-char filters. A second filtration is followed by adjustment of the pH of the glucose syrup to 4.7, by means of a small amount of hydrochloric acid (never exceeding 0.0047 per cent), reconcentration to proper gravity, and neutralization of the mineral acid by sodium acetate, leaving the pH at the proper figure. This is done to prevent inversion of cane sugar when the syrup is mixed with it in confectionery manufacture. The final syrup is about 45° Bé. and is clear and colorless.

Commercial glucose is not a single substance in solution, but a mixture of three: dextrin, maltose, and glucose. The bulk of the syrup on the market contains about 34 per cent of reducing sugar, essentially glucose, and calculated as such. It serves in the confectionery trade as a sweetening agent; it is also sold in small cans for consumption as a syrup in households.

By using more acid and heating in the closed converter for a longer period (30 minutes), the conversion to glucose is approximately complete. A starch solution rotates polarized light farther to the right than *d*-glucose; the fall in rotation has therefore become a means of following the progress of the conversion. The product after neutralization and filtration may then be made into a solid, by evaporating in two steps, as with cane sugar. In the first step, the syrup is produced, and this enters a single-effect vacuum pan, where it is concentrated to 42° Bé., with a content of 80 per cent glucose. The concentrated sugar liquor is run onto large tables where it solidifies; when cold, it is cut into slabs, and these are chipped into smaller pieces for shipment. This is corn sugar, also called grape sugar. It may be crystallized by seeding it with glucose crystals, called "dextrose" in the trade. The sugar is slowly agitated during crystallization, which is slow; after 90 to 100 hours, the crystals are centrifuged, and are then 99.5 to 100 per cent pure. This is "dextrose hydrate," perfectly white in color.

TABLE 79.—*Corn processed and sales of products from corn in the wet-process industry**

	1947
Wet-process grindings	139,273,000 bushels
Corn starch	1,509,289,000 pounds
Corn sugar	785,293,000 pounds
Corn syrup, unmixed	1,983,006,000 pounds
Dextrines	162,429,000 pounds
Corn oil, crude	40,630,000 pounds
Corn oil, refined	181,226,000 pounds
Gluten feed and meal	1,015,000 tons
Corn-oil meal	63,000 tons

* Bureau of Agricultural Economics, Division of Statistical and Historical Research; U. S. Dept. Agriculture. (The figures for sales approximate those for production.)

The syrup from the first step is "corn syrup unmixed" used in candy making, in baking, and in preserving; with the addition of cane sugar syrup, it becomes a table syrup, known for example as Karo.

The continuous hydrolysis of corn starch has been successfully performed on a pilot plant basis.[22] The three variables which influence the

[22] "The continuous hydrolysis of corn starch," J. E. Dlouhy and A. Kott, *Chem. Eng. Progress*, 44, 399 (1948).

design are holding time in the hydrolysis coil (see Fig. 194), the reaction temperature and the acid catalyst concentration; the latter lay between 0.030*N* sulfuric acid for dextrose, and 0.007*N* for paste. The hydrolysis coil was 324 feet long and 2.06 inches I.D. The holding period was varied from 15 to 25 minutes; "dextrose" (*d*-glucose), syrups, or pastes may be produced.

Both corn syrup and corn sugar are of industrial importance, as indicated in Table 79.

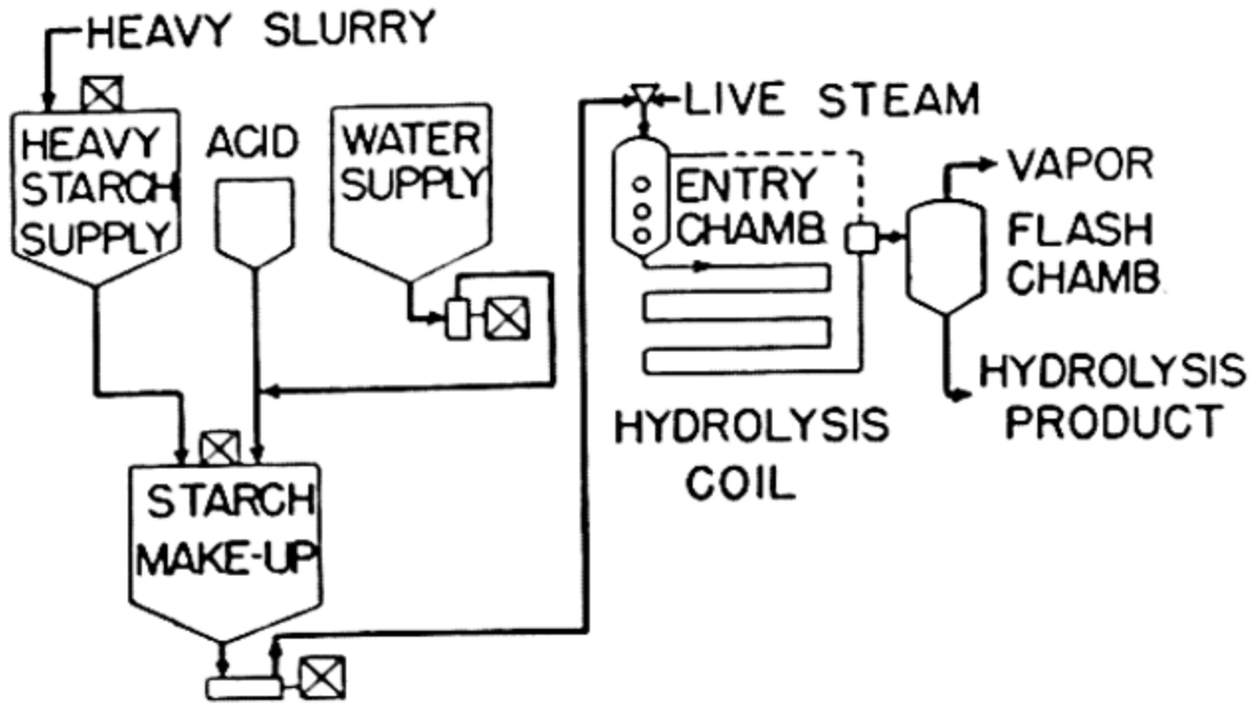


FIGURE 194.—Flow of materials in the continuous hydrolysis of corn starch. [Reprinted from *Chem. Eng. Progress*, 44, 399 (1948)].

OTHER PATENTS

1,849,998, production of sugar from dried sugar beet; 1,755,165, method of treating beet juice to produce sugar; 1,750,756, manufacture of corn starch; 1,792,088, manufacture of soluble starch, by sodium hypochlorite; 2,216,753 and 4, washed sugars; 2,216,755, treating sugars.

PROBLEMS

1. A cane sugar factory is grinding 85 tons of cane per hour. A mill extraction of 94.6 per cent of the sucrose in the cane is obtained. The boiling house recovery is 87 per cent and the sucrose percentage in the cane is 13.5. Calculate: (a) How many tons of sugar polarizing 97° is obtained per 24 hours? The 97° sugar is also 97 per cent sucrose. (b) How many tons of cane are required per ton of the 97° sugar? (c) What is the overall recovery?

On the *recovery of sucrose*. Between 86 per cent and 95 per cent of the sucrose extracted by the mills is recovered by the boiling house in the form of commercial sugar. The recovery obtained depends mainly on the purity of the juices and the efficiency of the equipment. The overall recovery of sucrose (i.e., sucrose in sugars % sucrose in cane) usually varies between 82 per cent and 90 per cent. The following example will serve to demonstrate the method of calculating the overall recovery of sucrose and the tons of cane required to manufacture a ton of commercial sugar.

	%
Sucrose Per Cent Cane	=13.2
Mill Extraction of Sucrose	=94.2
Boiling House Recovery	=88.2
Polarisation of Commercial Sugar	=96.5°

Then,

		%
Sucrose extracted per cent Cane	$=13.2 \times 94.2/100$	$=12.434$
Sucrose recovered per cent Cane	$=12.434 \times 88.2/100$	$=10.966$
Overall recovery	$=10.966 \times 100/13.2$	$=83.08$
(Or, overall recovery)	$=94.2 \times 88.2/100$	$=83.08$
Commercial Sugar per cent Cane	$=10.966 \times 100/96.5$	$=11.36$
(Or, Commercial Sugar per cent Cane)	$=83.08 \times 13.2/96.5$	$=11.36$
Tons of Cane required to manufacture one ton of Commercial Sugar	$=100/11.36$	$=8.80$ tons

2. Two tons of sugar beet containing 16 per cent sucrose are extracted. The recovery is 80 per cent. How many pounds of beet sugar are obtained? In order to precipitate the remaining sucrose, hydrated lime is added to the molasses, in an amount sufficient to precipitate all the sugar as tricalcium saccharate $3CaO \cdot C_{12}H_{22}O_{11}$. How much lime will you need?

Reading References

"The manufacture of sugar from the cane and the beet," T. H. P. Heriot, London and New York, Longmans, Green and Co., 1920.

"The sugar-beet in America," F. S. Harris, New York, Macmillan Company, 1919.

"Agricultural Yearbook for 1923," U. S. Department of Agriculture, Washington, D. C., pp. 151-228.

"Cane sugar and its manufacture," H. C. Prinsen Geerligs, London, Norman Rodger, 1924.

"Cane-juice liming and clarification," R. H. King, *Ind. Eng. Chem.*, 23, 954 (1931).

"The celotex and cane-sugar industries, bagasse or sugar a by-product?" E. C. Lathrop, *Ind. Eng. Chem.*, 22, 449 (1930).

"Outline of the activities at Argo," published by the Corn Products Refining Company, Argo, Illinois.

"Handbook for cane sugar manufacturers and their chemists," G. L. Spencer, revised by G. P. Meade, New York, John Wiley and Sons, Inc., 1945.

"Filtration of phosphate-defecated affination sirup," H. I. Knowles, *Ind. Eng. Chem.*, 34, 422 (1942).

"Advantages and disadvantages of continuous clarifiers for refining," J. M. Brown and W. A. Bemis, *Ind. Eng. Chem.*, 34, 419 (1942); see articles on related topics in pages 403 to 429, same reference.

"Technology for sugar refinery workers," Oliver Lyle, London, Chapman & Hall, Ltd. 1941.

"Cane sugar," Noel Deerr, London, Norman Rodger.

"Polarimetry, saccharimetry and the sugars," Circular 440, U. S. Dept. of Commerce National Bureau of Standards, 1942.

"Recent Improvements in the Simple Clarification for Raw Sugar Production," J. G. Davies, Memoir, Dept. of Sugar Technology, The Imperial College of Tropical Agriculture, Trinidad, B.W.I.

"The Calcium Phosphate precipitate in limed Cane Juices. Hugo P. Kortschak. *International Sugar Journal* (1944), p. 182.

"Working with the Carbonation Process," J. Rault, *International Sugar Journal* (1947), pp. 42-44.

"Processing of Final Crystallizer Massecuites." G. E. Stevens, *International Sugar Journal* (1945), pp. 158-162.

"Refining Raw Cane Sugar in the Factory," J. Campbell Macdonald, *International Sugar Journal* (1945), pp. 40-44.

"Sugar Refining in the Beet Sugar Factory," J. Campbell Macdonald, *International Sugar Journal* (1944), pp. 294-297.

"Sugar the Unknown," R. C. Hockett (Sugar Research Foundation, N. Y.). American Chemical Society, April, 1944, Cleveland Meeting.

In 1941, there were produced in the United States 1,404 million barrels of crude petroleum. In every succeeding year, there was an increase in the production; in 1946, the figure stood at 1,733,424,000. The consumption has been about equal to the production. It is estimated that in 1952, the demand for United States consumption will be 2,600 million barrels.

Petroleum and its products have become necessities in the modern world. In the hour of danger in the war years, the nation looked to the oil industry, its managers, engineers, chemists and operators, for specialized products direly needed, and not in vain. It is again trusting the same groups to find new oil, more oil, to develop new processes, and better existing ones, so that the future needs of the nation may be met.

Chapter 24

Petroleum and Its Products; Synthetic Liquid Fuels; Petrochemicals

Petroleum and Its Products

When first obtained from the ground, before refining in any way, petroleum (rock-oil) is called "crude oil." It occasionally shows itself at the surface, through seepage; it usually occurs at moderate depths; in some cases it must be sought by drill holes over a mile deep. When such a drill hole reaches an oil basin, the oil is frequently forced out under enormous pressures; gas, salty water, and sand usually accompany the oil. After a period which varies considerably, the flow becomes quieter; after some months it does not gush at all, and the oil must be pumped out; finally, no oil is obtained even by pumping; the well is dry. New wells are therefore constantly being sought. The oil prospector chooses lands possessing a subsoil which has characteristics indicating petroliferous strata; these characteristics vary in different fields, and in no case is it beyond doubt that a drill hole will reach oil. The search for oil is supplemented by accidental discoveries, in the course of drilling for water, for example. Where natural gas occurs, it is reasonable to prospect for oil;* it is by no means certain that oil will be found, but since petroleum consists of a mixture of hydrocarbons, the lighter ones such as methane, CH_4, and ethane, C_2H_6, may have escaped, in part, leaving the main body of liquids and solids not very far away. The heaviest hydrocarbons, beginning for example, with eicosane, $C_{20}H_{42}$, which melts at blood temperature, are solid; the intermediate ones liquid.

Discovery of Oil. It was not the genius of man which discovered oil, but rather the oil which revealed its presence and forced itself upon his attention, by seepages which frequently coated small rivers, as in Pennsylvania; by contaminating brines, much to the disgust of the early (1806) salt refiners, like the brothers Ruffner along the Kanawha river in West Virginia; in the escaping gas, rich in vapors and known for centuries, as in the Baku penin-

* The Rodessa field, Caddo Parish, in Louisiana, was a gas field for many years; only in 1935 was it discovered to carry oil.

sula, where the "eternal" fire gave a powerful support to religious cults (Zoroasters).[1] Only in more recent times, especially in the three decades past, has a more intensive search taken place, partly because the evident clues had been exhausted, and partly because petroleum has become a necessity to national as well as to civil life. To the study of the soil for indications of petroliferous strata, which has already been mentioned, scientific methods were added: the revival of the anticlinal theory, the measurement of temperature in adjacent wells in order to locate the anticlinal axis; gravitometry, including seismic or sonic apparatus; the electric log; and the magnetometer.[2]

The seismic method for underground exploration is an adaptation of the study of low-lying, deeply buried rock formations, by the echo characteristics of time and direction of an artificial vibration, such as the explosion of a charge of dynamite; it is called the seismic reflection method. A portable seismometer is set firmly on hard ground; it consists of a post bearing a long pointer rigidly fastened to it, and a heavy weight suspended from an arm. The post moves with the vibrations of the ground; the pointer magnifies them, and throws a point of light on the face of the weight which, by virtue of its inertia, does not respond to the vibrations. A moving-picture camera, set in rubber, records the path of the light; the rate of travel of the film gives the measure of time in thousands of seconds. A charge of dynamite, say 11 pounds, at a depth of 95 feet is set off, and the first vibration as well as the subsequent reflections from the low-lying rock formation are recorded. The time for the reflection to travel upward gives the depth; thus, in one case, two and 365/1000ths seconds indicated 18,000 feet. The slope of the strata is given by the shape of the curve. Many such records are made in order to plot an area.[3]

More recent still are a geochemical method, the "halo method," and an electrical method, such as the Eltran. In the geochemical method, soil surveys[4] are conducted by measuring hydrocarbon content and mineralization in subsoil samples which are gathered with an ordinary auger. Eight analyses per square mile are preferred. The hydrocarbons are ethane, measured in parts per billion of soil, or the more concentrated liquid or waxy hydrocarbons. The significant high values, determined by statistical means, are plotted. If they form a pattern such as an aureole or halo, the area is positive and the petroleum deposit is roughly outlined by the pattern. The mineralization figures are also plotted, and give in a number of published surveys a similar pattern for the same area.

Petroleum is found only in sedimentary rocks, and has its origin in the remains of plants and animals,[5] which accumulated with clays and muds

[1] P. 478 and 474, in "Outstanding features of petroleum development in America," by David White, *Bull. Am. Assoc. Petroleum Geologists,* 19, 469-502 (1935).

[2] *Ibid.,* 501.

[3] In part from a radio broadcast by Dr. John P. Buwalda, California Institute of Technology, in a series on Recent Developments in the Geologic Sciences, under the name, "Searchers of the Unknown," Jan. 4, 1936.

[4] Geophysical Service, Inc., Dallas, Texas, publishes a bulletin called "Soil Surveys."

[5] There have been many theories for the formation of petroleum deposits in the ground. Among the earlier ones was that of Engler who referred the formation of petroleum to a store of fatty remains of all kinds of life, but especially animal life; his

along the seashore. At a later geologic period, the droplets or gas migrated from the source muds into a "reservoir" rock, chiefly sandstone. The strata were lifted and warped, forming arches (anticlines) and troughs (synclines), from one mile to several miles in width. Oil is found in the anticlines, having risen above the water; it may also be found in synclines, if the upper space (to the neighboring anticlines) is filled with the still lighter gas, also formed from these deposits, and tapped as natural gas. An oil or gas pool is not a subterranean pond, but merely an accumulation of petroleum or gas in rock pores. The container rock is of a highly porous type[6] in which the interstices are such as to permit the oil, gas and water to move freely; the dense or non-porous retainer rock prevents the escape of the oil or gas from the container rock. The petroleum generally contains large amounts of gas in solution, under pressure.

It was in 1859, at Titusville, Pa., that Colonel Drake sank his now famous well; it was 59½ feet deep. Since then, many wells have been driven, and the depth has steadily increased. In 1946, a total of 26,991 wells were drilled in the United States, of which 15,851 were oil wells, 3,090 were gas wells,[7] and 8,050 dry holes (Minerals Yearbook). In 1947, 33,098 wells were drilled, and in 1948, 38,750 (estimated). A depth of 19,473 feet has been reached and now passed (May 5, 1949) in the drilling of a well at Pacific Creek. A producing well over 15,000 feet deep is on record; in 1941, there were 23 wells over 13,000 feet in depth.

The producing oil wells in the United States on January 1, 1946, totalled 415,750, and the average production over the year per well per day was about 11.4 barrels. The cost of a 10,000-foot well is $250,000 or more. Depth drilling has been helped by the development of rotary drilling; several new chemical agents, the application of acids,[8] and the use of special muds[9] have contributed.

When first tapped, the well may be a gusher, with many thousands of barrels a day; this output begins to decrease at once, and gradually tapers

---

opinion was based on laboratory experiments with menhaden oil, from which he produced a petroleum-like substance. C. Engler, *Ber. Deutschen Gesellschaft*, 21, 1816 (1888). Among the present workers, Alfred Treibs assigns to plants the dominant rôle in forming petroleum, to animal remains a secondary rôle. His statement is based on the spectroscopic study of the light absorption of petroleums, in which he thus identifies and estimates quantitatively porphyrins of chlorophyll origin in a high percentage, while he also finds porphyrins of hemoglobin origin, but in much smaller amounts. *Ann.*, 510, 42 (1934). A brief summary of the older theories will be found in "The examination of hydrocarbon oils and saponifiable waxes," D. Holde, tr. by Edward Mueller, New York, John Wiley and Sons, 1922.

[6] The porosity of a rock is defined as the property of containing interstices or openings, which may vary in size from caverns to subcapillary pores.

[7] In some cases, it is possible that an upper pool, which has been pumped out, is underlain by a lower pool. The Fox pool, Oklahoma, at the 2000-foot level, producing since 1916, was "on the pump" in 1935; in October of that year a new well, 8088 feet down, brought in a new producing pool, 6000 feet under the original one. It was gusher, with 8 to 10 thousand barrels a day. "The field that came back," C. E. Savage, *The Lamp*, February, 1936.

[8] "Science goes down an oil well," J. Arthur Sohn, *The Lamp*, December (1936).

[9] "Taylor-made mud," *The Lamp*, June 1946, p. 17; "Drilling muds pose chemical problems," W. T. Cardwell, *Chem. Industries*, 61, 988 (1947).

off until a pump is needed to bring up the oil. A life of 20 years is a rough estimate for a newly tapped oil-bearing formation.

Petroleum Reserves. Taking petroleum from the ground means subtracting it from a finite store: less oil is left for the next generation. The rate of crude oil production has been rising, and even now with the war over, it continues to do so.

TABLE 80.—*Production of crude oil in the United States expressed in units of 1000 barrels per year.*

1942	1943	1944	1945	1946	1947*	1948*
1,386,645	1,505,613	1,677,904	1,713,655	1,744,424	1,856,025	1,987,425

* Estimated.

In past years, it was possible to discover new oil-bearing formations, and to extend known fields, in amounts sufficient to balance and generally exceed the oil removed. At the present time (1948) the proved reserves are still ample, but there are disturbing factors. Thus there is concern over the

TABLE 81.—*Proven petroleum reserves* in the United States†*
(December 31, 1947 and 1948).

	1947	1948
Crude petroleum	21,487,685,000 Barrels	23,280,444,000
Natural gas liquids	3,253,975,000	3,540,783,000
Total	24,741,660,000	26,821,227,000

* Proved reserves: oil estimated to be recoverable by the production systems now in operation.
† Report of the American Petroleum Institute Committee on Petroleum Reserves.

TABLE 82.—*Proven petroleum reserves of the world (January 1, 1946).**

	Barrels
United States	20,827,000,000
Central and South America	8,343,000,000
Eastern Hemisphere	29,127,000,000
Middle East	20,968,000,000
Far East	1,156,000,000
Total	59,453,000,000

* Mainly from *The Lamp*, April, 1946.

diminishing rate of new discoveries; the proved reserves—that is, known reserves in well established formations—might diminish, while on the other hand, the amount of oil removed continues to increase year by year. Another consideration is that of exports and imports. In the past, the latter were less than exports of crude oil, but now they are greater. For example, in 1946, 86 million barrels of crude were imported, and only 41 million barrels exported. It might be noted also that finding oil and drilling wells now are far more costly than a decade ago. The military want to feel that there is a safe margin of oil supplies against a sudden emergency. The results are (1) the development and constant improvement of means for conserving oil, wasting none, and leaving the least possible unextracted in the formation, and (2) supplementing these means to conserve by developing other sources of motor fuel, such as the distillation of oil shales, and (more promising) the manufacture of synthetic liquid fuel from natural gas (see later).

Means of conserving oil have commanded increased attention and study. One is to reduce or abolish waste caused by too-rapid removal of oil from a formation; this is accomplished by excessive lowering of the potential (pressure) of the well. Much is being done by state regulations, by proration, by the unit operation of pools.[10] Another is the more complete extraction of oil from the oil sands. It should be explained that rarely is as much as 50 per cent of the total oil in a formation extracted; more often, it is 30 per cent or less. In order to recover the residual oil, the formation may be flooded with water, which drives the oil toward the well in which a pump may be working. For this method to be successful, the ground formations must be favorable. Much secondary oil is recovered also by pumping gas into the formation (repressuring). Flooding with water has given good results in Pennsylvania, which produces a premium crude, and elsewhere; on the other hand in Ohio, for example, the results were poor.[11]

The oil fields in the United States are the most important in the world. In many localities, oil derricks dot the landscape, for example, between Pittsburgh, Pa., and Wheeling, W. Va.; in Los Angeles, there is an oil field within the greater city limits; farther north, in the Ventura field, derricks are built over the sea. The search for oil has now extended to the continental shelf,[12] which is the submerged border of the continental masses, so that more and more equipment for withdrawing oil will be built over seawater. The relative importance of the several states as oil producers is shown below.

TABLE 83.—*Production of crude petroleum in the United States in 1946 for the fourteen leading states.**

	Barrels		Barrels
Texas	760,505,000	New Mexico	36,860,000
California	315,179,000	Arkansas	28,375,000
Louisiana	143,303,000	Mississippi	24,216,000
Oklahoma	134,497,000	Michigan	17,074,000
Kansas	97,218,000	Pennsylvania	12,996,000
Illinois	75,297,000	Colorado	12,016,000
Wyoming	38,304,000	Kentucky	10,578,000

Total 1,733,424,000 barrels; average value per barrel at the well $1.41.

* "Minerals Yearbook," 1946.

Valuable oil regions occur in Russia (on the Baku peninsula in the Caspian Sea), in Rumania,[13] Galicia, Mexico, Venezuela, the Dutch East Indies,[14] and in the Middle East (Iraq, Iran, and Saudi Arabia). Fig. 195 shows these and other fields in the Middle East, as well as the route for the projected additional pipe line. The production figures in Table 84 indicate,

[10] A brief treatment of laws and regulations concerning crude oil production will be found in *Minerals Yearbook*, 674–5 (1936); *Minerals Yearbook*, 771–794 (1935). On conservation in general, read: "Probable petroleum shortage in the United States and methods for its alleviation," L. C. Snider and B. T. Brooks, *Bull. Am. Ass. Petroleum Geologists*, 20, 15 (1936).

[11] See graph on p. 31, *Bull. Am. Assoc. Petro. Geologists*, 20 (1936).

[12] "Continental shelf," *The Lamp*, March 1947, p. 19, with a map.

[13] *The Lamp*, June 1945, p. 1 to 7, with a map of middle Europe showing oil wells and refineries.

[14] *The Lamp*, June-September 1948, p. 19, with a map.

at least in a general way, the relative importance of some of the foreign fields.

Transportation of Crude. Crude petroleum is transported in large part by pumping it through pipe lines; the oil is sent great distances in this way, avoiding the high freight bill which it otherwise would incur. The crude oil travels through especially constructed trunk pipe lines laid in the ground

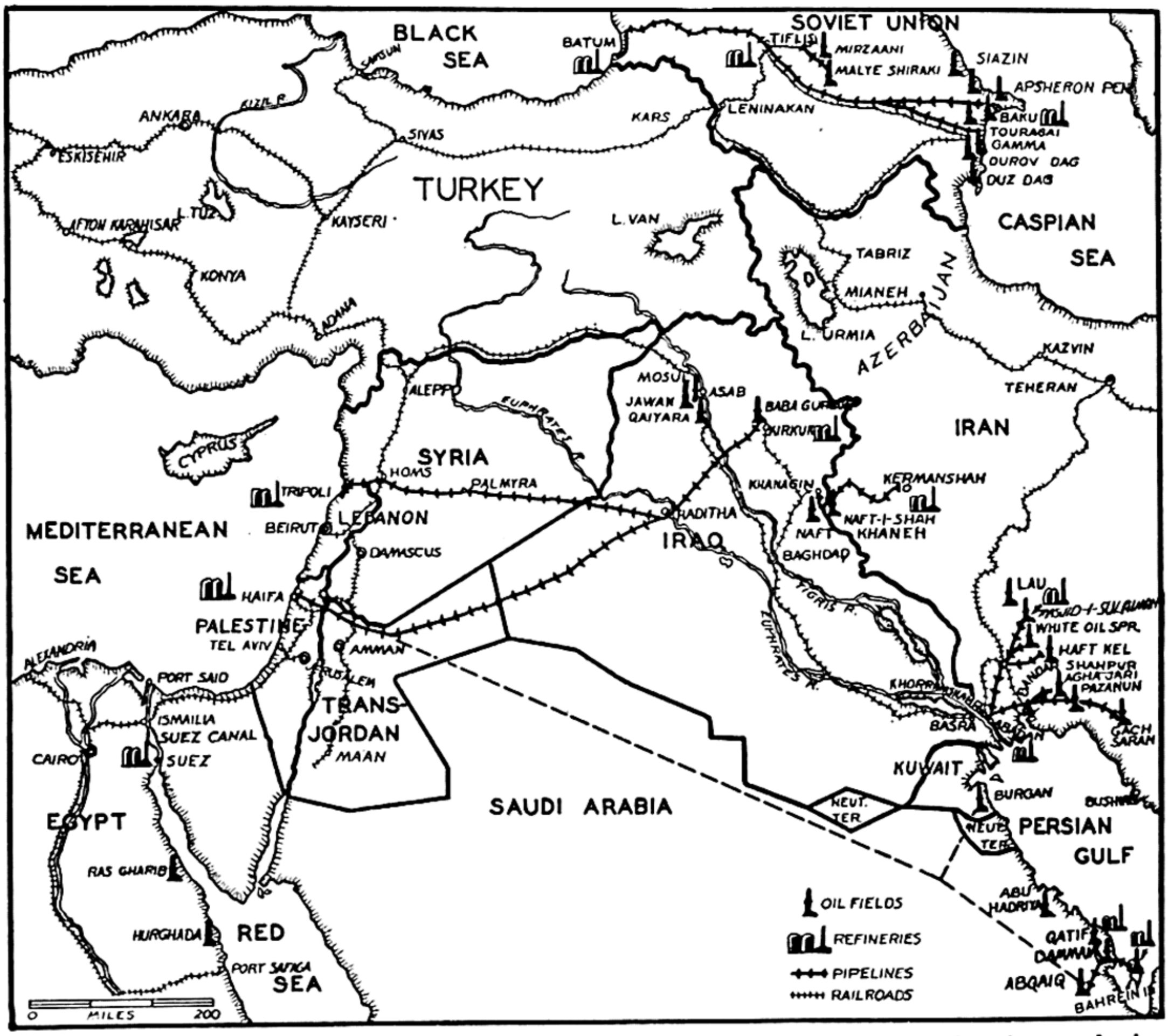


FIGURE 195.—Map of the Middle East, showing location of oil wells, refineries, and pipe lines. The new proposed pipe line now under construction, 30 inches in diameter half way, 31 inches for the other half, and 1,000 miles long, is shown as a dotted line from Abqaiq to Haifa. It is estimated that in 1952 the Middle East will produce 500,000,000 barrels a year. (Drawn from a map in the *New York Times*, Dec. 22, 1946.)

along a purchased right of way thirty feet wide, in sections 75 miles long or more. Each section has its own pumping station and storage tanks, and the right of way is patrolled for leaks. Counting pipe line 2-inches to 16 inches in diameter, there are 125,000 miles of lines [15] in the United States; similar lines which transport refined products come to 15,000 miles more. The capacity of an 8-inch line under a pressure of 400 pounds is 25,000 gallons

[15] "Pipelines," *The Lamp* (Jan. 1947), p. 5, with a map. For wells and pipelines in Alaska and the Yukon, see *The Lamp*, Oct. 1943, p. 3, with a map. A large map of the oil pipe lines may be obtained from the *Oil and Gas Journal*, Tulsa, Okla., for a nominal price. The same map on its other side shows the natural gas trunk lines.

TABLE 84.—*Crude petroleum produced in principal countries of the world (in barrels of 42 gallons each) in 1946.**

North America		1,810,710,000
Canada	7,668,000	
Mexico	49,235,000	
Trinidad	20,233,000	
United States	1,733,424,000	
Others	150,000	
South America		446,417,000
Venezuela	388,486,000	
Colombia	22,118,000	
Argentina	20,604,000	
Peru	12,456,000	
Ecuador	2,323,000	
Europe		212,842,000
U.S.S.R.	164,000,000	
Rumania	31,206,000	
Asia		271,129,000
Iran	146,614,000	
Saudi Arabia	59,944,000	
Iraq	35,665,000	
Bahrein Island	8,010,000	
Sakhalin	6,000,000	
Kuwait	5,931,000	
Netherland Indies	2,100,000	
[Netherland Indies	48,294,000 in 1943]	
Africa (mainly Egypt)		9,090,000
World total		2,750,190,000

* "Minerals Yearbook."

a day. When a ridge is to be crossed, the line is so disposed that one leg is downhill, so that by its syphon effect it will help pull the oil up the hill. In this way crude oil from Oklahoma reaches Bayonne, N. J., and Marcus Hook, Pa.; while Texas crude can be sent to Chicago (Whiting, Ind.) or Buffalo, N. Y. A 12-inch pipe line 237 miles long, running from South Portland, Me., to Montreal, operated by eight pumping stations, has a capacity of 60,000 barrels daily of light crude oil. No pipe line crosses the Rocky Mountains. In the pipe lines, the shipments of various types are not separated, but the head of the next is allowed to mix with the tail of the previous one. The oil dispatchers sort them out; the mixed portion is separated and serves for inferior purposes. The other modes of transportation are by boat (oil tankers), by tank car, and tank truck. In 1946, 409 million barrels were transported by boat of which 86 million were of foreign origin; 1,290 million barrels by pipe lines, and 38 million by tank cars and trucks.

In World War II, multiple 3-inch pipe lines of light steel construction were laid across the water from England to France,[16] and extended finally to Frankfurt in Germany. Previous to that but also during the war, a pipe line grid was built from oil-ports to London and to other centers in England itself.[17] Marine pipelines permitted a tanker to feed the tanks of a terminal station, from which it traveled further by emergency lines.

[16] "Pipelines powered our blitz," *The Lamp*, Dec. 1944, p. 7.
[17] "The oil pipeline," The Industrial Chemist, 21, 66 (1945).

TABLE 85.—*Classification in 7 classes of petroleum crudes, according to their "base," from the distillation-analysis of 800 samples from all over the world* [R. I. 3279, *U. S. Bureau of Mines, E. C. Lane and E. L. Garton (1935); condensed*].

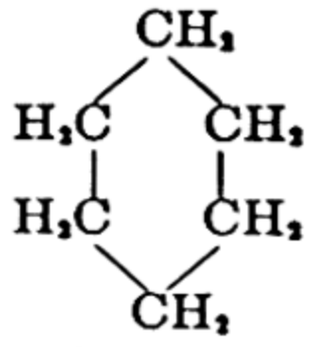
	A Paraffin base oil (wax-bearing)	B Paraffin intermediate base oil (wax-bearing)	C Intermediate Paraffin base oil (wax-bearing)	D Intermediate base oil (wax-bearing)	E Intermediate Naphthene base oil (wax-bearing)	F Naphthene intermediate base oil (wax-bearing)	G Naphthene base oil (wax free)
A.P.I. gravity	49.7°	39.2°	29.5°	39.6°	15.3°	29.5°	24.0°
Specific gravity	.781	.829	.879	.827	.964	.879	.910
Pour point	below 5° F.	below 5° F.	40° F.	below 5° F.	40° F.	below 5° F.	below 5° F.
Per cent sulfur	0.1	0.28	0.32	0.33	3.84	0.16	0.14
Saybolt Universal viscosity 100° F.	34 seconds	41	120	39	4000	47	55
Color	green	greenish-black	greenish-black	green	brownish-black	greenish-black	green
Distillation 1st drop	93° F. (34° C.)	91° F. (33° C.)	176° F. (80° C.)	84° F. (29° C.)	280° F. (138° C.)	138° F. (59° C.)	315° F. (157° C.)
Distillates:							
Gasoline and naphtha	45.2%	32.0	5.8	38.6	2.9	21.3	1.1
Kerosine	17.7%	17.2	nil	4.9	4.5	nil	nil
Gas oil	8.3%	10.6	27.8	17.3	10.6	34.6	55.5
Nonviscous lubricating	9.8%	10.9	20.4	9.4	8.6	10.4	14.2
Medium lubricating	3.4%	5.2	9.2	6.3	6.7	7.0	4.7
Viscous lubricating	nil	nil	nil	nil	1.020	4.7	11.6
Residuum	14.7%	23.5	36.4	22.1	58.4	21.4	12.7
Distillation loss	.9%	.6	.4	1.4	1.9	0.6	0.2
Carbon residue of residuum	1.1%	6.2	6.9	7.3	18.2	8.7	4.5
Carbon residue of crude	0.2%	1.5	2.5	1.6	10.6	1.9	0.6
Key fraction No. 1. (250-275° C.) 482-527° F., 750 mm. pressure.							
Per cent cut	6.8%	6.5	7.1	5.8	5.1	10.1	19.6
A.P.I. of cut	44.7°	40.6	36.4	37.0	37.0	30.2	27.9
Key fraction No. 2. (275-300° C.) 527-572° F., 40 mm. pressure.							
Per cent cut	4.4	5.7	9.0	4.9	8.2	6.0	7.3
A. P. I. of cut	34.4°	29.3	30.0	24.9	19.5	24.0	16.5
Viscosity at 100° F.	110 seconds	120	120	165	240	230	over 400
Cloud test, in °F.	90	90	90	80	70	90	below 5

If key fraction No. 1 reads 40.0° A.P.I. or lighter, the lower boiling fractions of the oil are paraffinic; if it reads 33.0° A.P.I. or heavier, they are naphthenic; if its gravity lies between 33.0° and 40.0° A.P.I., they are intermediate.

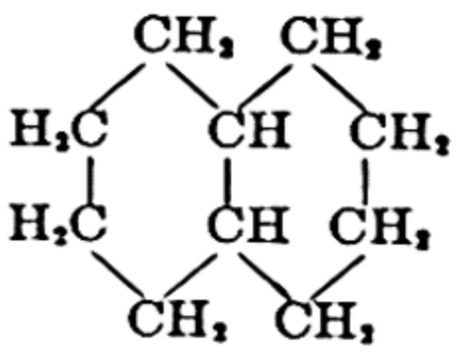
If the gravity of key fraction No. 2 is 30.0° A.P.I. or lighter, the higher-boiling fractions of the oil are paraffinic; if it is 20.0° A.P.I. or heavier, the fractions are naphthenic; while if the gravity lies between 20° and 30° A.P.I., the fractions are intermediate.

Refined Products. Formerly oil was burned as such for its fuel value, and to a small extent this is still done, but by far the greater amount is refined, to give specialized, hence more valuable products, and only that portion which cannot be made to yield any of the more valuable products is burned under boilers (fuel oil, bunker oil). On distilling crude oil, there are obtained: gases, which are processed or burned for their heat values; gasoline, for internal combustion motors with spark firing; solvent naphthas, kerosine, gas oil, Diesel oil, fuel oil, lubricating oil, paraffin (hard wax), petrolatum (soft wax), road tar, coke, and other products. The ultimate analysis of crude petroleum would indicate from 83 to 85.5 per cent carbon, 11.0 to 14.2 per cent hydrogen, and small and varying amounts of nitrogen, oxygen and sulfur.[18] The crude oil must be separated from any water it may entrain; certain crudes are in the form of an emulsion with the water, and this emulsion must first be broken before separation can take place.

Classification of Crudes. An eminently satisfactory classification of crudes has been developed by the U. S. Bureau of Mines; the main features are given in Table 85. Class A comprises the paraffin-base crudes, which are wax-bearing; these contain mainly paraffinic hydrocarbons in all their fractions; their residue in the still becomes the much-sought after "cylinder stock." Straight-distilled gasolines from this crude would be paraffinic, and have "knocking" properties. Naphthene base oil, class G, contains mainly naphthenes, that is, cyclic compounds which are saturated, with side chains both naphthenic and paraffinic. Naphthene base and intermediate naphthene base, class E, may contain much black, brittle, almost infusible asphaltic material, although they often do not; when they do, they fit the old description of asphalt-base oils. Naphthenes are hydrocarbons of the C_nH_{2n} series, rich in hydrogen, with ring formation; they carry side chains



Hexahydrobenzene
(a naphthene)



Decahydronaphthalene
(a naphthene)

(not shown below) which may be naphthenic or paraffinic. The paraffins are the straight-chain, or branched-chain hydrocarbons; iso-octane, normal heptane, cetane, presented farther on, are examples. The naphthenes merge

[18] *Pet. Ref.*, 25, 232 (1946).

Origin of samples in Table 85:

A. West Virginia, Ritchie Co., Lost Run field
B. Oklahoma, Lincoln Co., Chandler field
C. Louisiana, Webster Parish, Cotton Valley field
D. Oklahoma, Seminole Co., Seminole field
E. Wyoming, Park Co., North Sunshine field
F. Texas, Austin Co., Raccoon Bend field
G. Texas, Refugio Co., Refugio field

Each of these samples is typical of the class it represents. The seven classes listed in the table are:

A. Paraffin base; distillates paraffinic throughout
B. Paraffin-intermediate base: light fractions paraffinic, heavy fractions intermediate
C. Intermediate-paraffin base: light fractions intermediate, heavy fractions paraffinic
D. Intermediate base: distillates intermediate throughout
E. Intermediate-naphthene base: light fractions intermediate, heavy fractions naphthenic
F. Naphthene-intermediate base: light fractions naphthenic; heavy fractions intermediate
G. Naphthene base, distillates naphthenic throughout.

into oils rich in aromatics, that is, derivatives of benzene and higher members of the series C_nH_n, which also has an endless assortment of side chains.

The crudes differ also in the relative amounts of lower- and higher-boiling constituents: some are so thick that they barely pour; others are as fluid as kerosine. This is well brought out in Table 85; in fact, one of the purposes in giving it is to answer precisely the question: how much gasoline does crude oil contain? The amount varies, but definite figures are now presented. An overall yield will be found elsewhere in the chapter.

The greatest demand is for gasoline, and in order to increase the supply of this material, the higher-boiling hydrocarbons are heated to an excessive temperature which causes them to decompose into more volatile, lower-boiling hydrocarbons, such as in gasoline; the operation is called "cracking," namely, cracking into smaller molecular fragments.

Exact boiling points and densities cannot be given, but the following may serve as guides:

Gasoline has a density of 55-60° Bé.,[19] and boils at 100-400° F. (37-8-204° C.).
Kerosine has a density of 40-45° Bé., and boils at 400-600° F. (204-315° C.).
Fuel oil varies greatly; it is sometimes 36-40 Bé., boiling range 400-600° F. (204-315° C.).
Lubricating oils have a density of 28° Bé., for the lightest engine oil, to very high densities.

The term *naphtha*, generally with a modifying adjective is in frequent use in the refinery. Thus the refiner speaks of light naphtha and heavy naphtha, which are two he mixes, in proportions varying with the weather, to produce gasoline. Other naphthas are: precipitation naphtha, with boiling range 122-266° F.; V. M. & P. (Varnish Makers and Painters') naphtha, 210-325; Stoddard solvent (Cleaners' naphtha), 300-400.

Refinery Operations

The Bubble Tower. Crude oil is distilled in a tall plate column, continuously operated, called the bubble tower; it is capable of separating at once the several grades, in the form of side cuts, besides removing volatiles overhead, and non-volatile residues as bottoms. The oil is heated in a separate furnace called the "oil heater," and introduced into the tower at a point some distance from the bottom, accompanied by superheated steam.

The bubble tower is a fractionating device; the liquid charge on each of its plates (often 30 or 40) differs in composition. Each plate has a number of small chimneys for the rising vapors, covered with bells or caps which deflect the vapors and force them to bubble through the liquid on that plate. Toward the top of the column, the liquids on the plates become richer in the more volatile constituents; toward the bottom, they become richer in the less volatile constituents. The vapors bubbling through the liquid on their way up lose some of their less volatile constituents, and acquire some of the more volatile constituents of the liquid. Given time enough, the two come to equilibrium—an ideal which cannot be realized in a commercial device. Liquid constantly overflows from one plate to the one next below, through a

[19] Bé. scale here is the scale for "lighter than water," *see* appendix.

sealed leg, in a manner which insures that only the well bubbled liquid can leave (Fig. 197). The liquid forms by condensation of vapors, but a major part of it is the "reflux," *i.e.*, of a portion of each cut which, after stripping, is cooled and returned to the tower at a selected level. The bubble tower action has been defined "as a washing process in which a rising stream of hot vapor is washed by a descending stream of cold liquid called reflux." [20]

Every detail of the bubble tower is designed with the utmost care. For example, the "deck space" (the distance between plates) should be sufficient

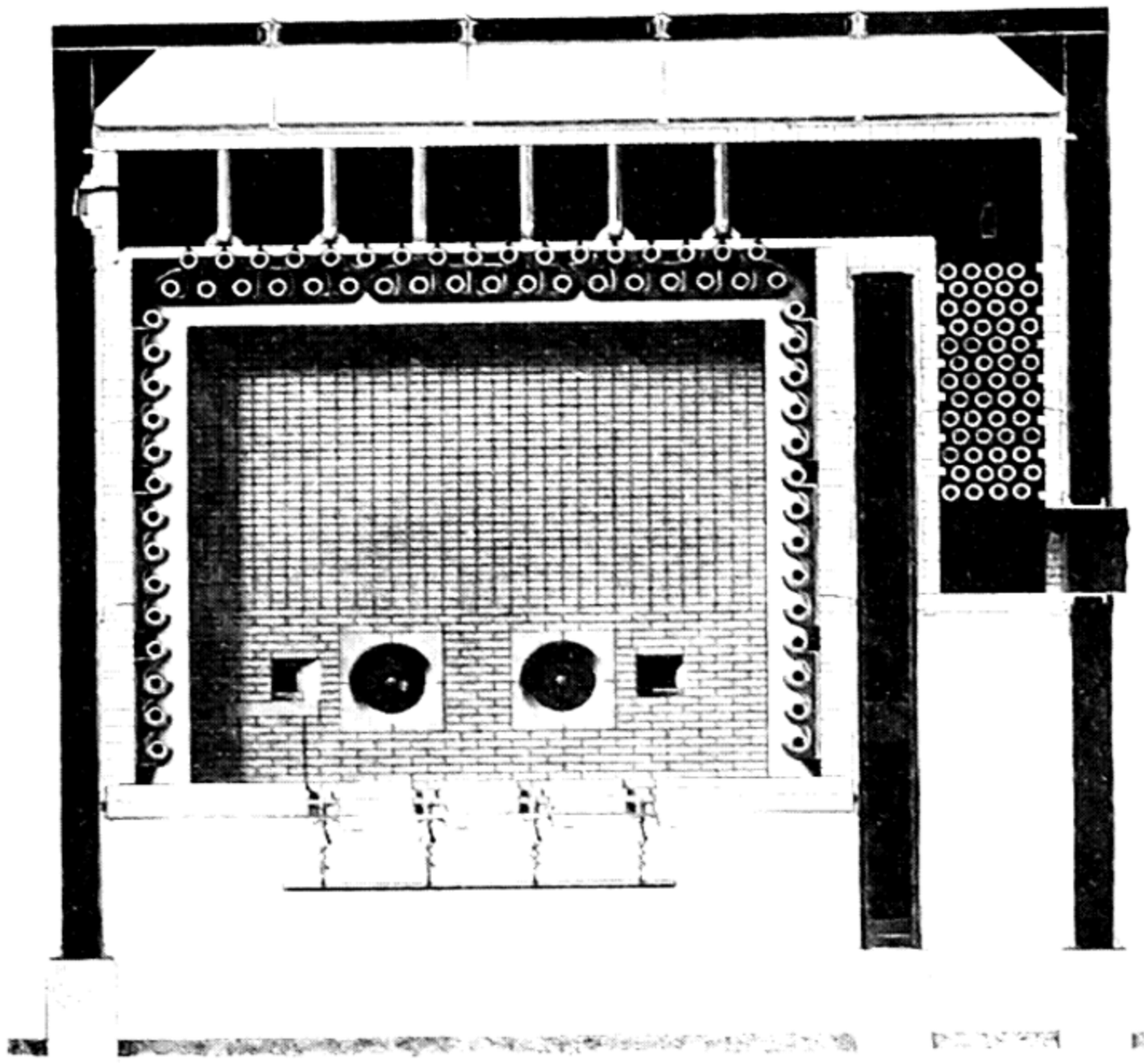


FIGURE 196.—Vertical cross section through an oil heater with single combustion chamber which may be fired either from the hearth with gas fuel, or from the end wall with oil. The fire gases rise to the plenum chamber at the top, then travel downward over the 52 convection tubes in the center. (Courtesy of Lummus Co., N.Y.)

to allow the vapors to disengage themselves from the droplets and films of liquid; it varies from 10 to 24 inches. The number of plates is determined by calculations checked by results. The vapor velocity is held at maximum; it is too high if it forces the liquid off the plates; 2 linear feet per second is average, 3.5 feet is high. A bubble tower handling 5,500 barrels of crude per day, in one refinery, is 92 feet high and 6 feet in diameter; it is well lagged to preserve heat. The pressure is essentially atmospheric.

As the side cuts are withdrawn, their fractionation is not complete, and must be supplemented by a small column called the stripper, one for each cut, in which the cut is freed by steam from all more volatile components than its set standard. A tower unit would be called efficient if the gasoline fraction had an endpoint of 400° F. and the kerosine an initial boiling point of 400° F. An overlap of 25° F. would not be bad; an overlap of 50° F. would be poor fractionation.

The capacity of a bubble tower depends upon its diameter and height; its

[20] Pennsylvania Grade Crude Oil Association, Bulletin II.

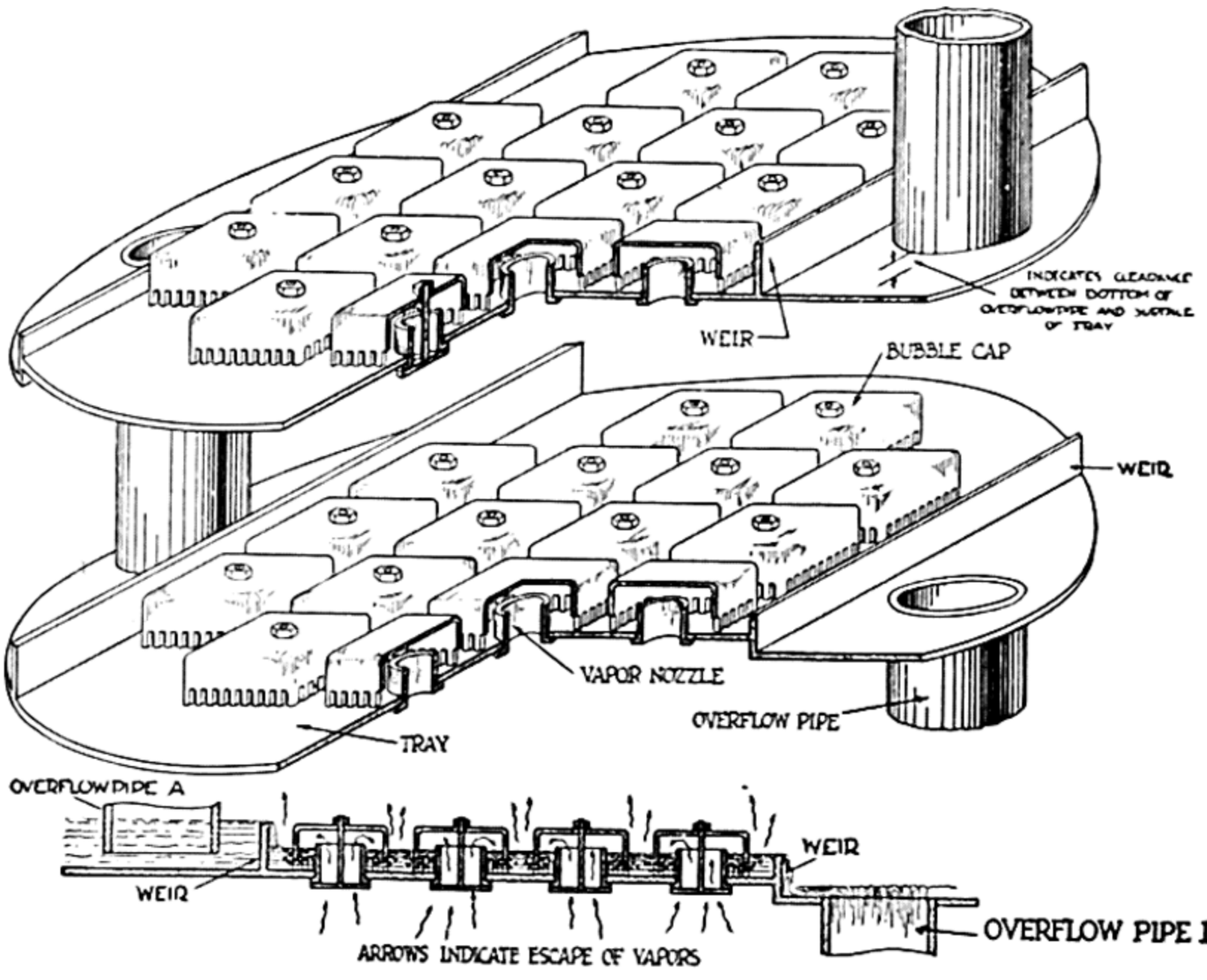


FIGURE 197.—Two plates in a bubble tower, showing the domes or bubble caps, the overflow or rundown pipes, and the weirs. (From the Pennsylvania Grade Crude Oil Association, Oil City.)

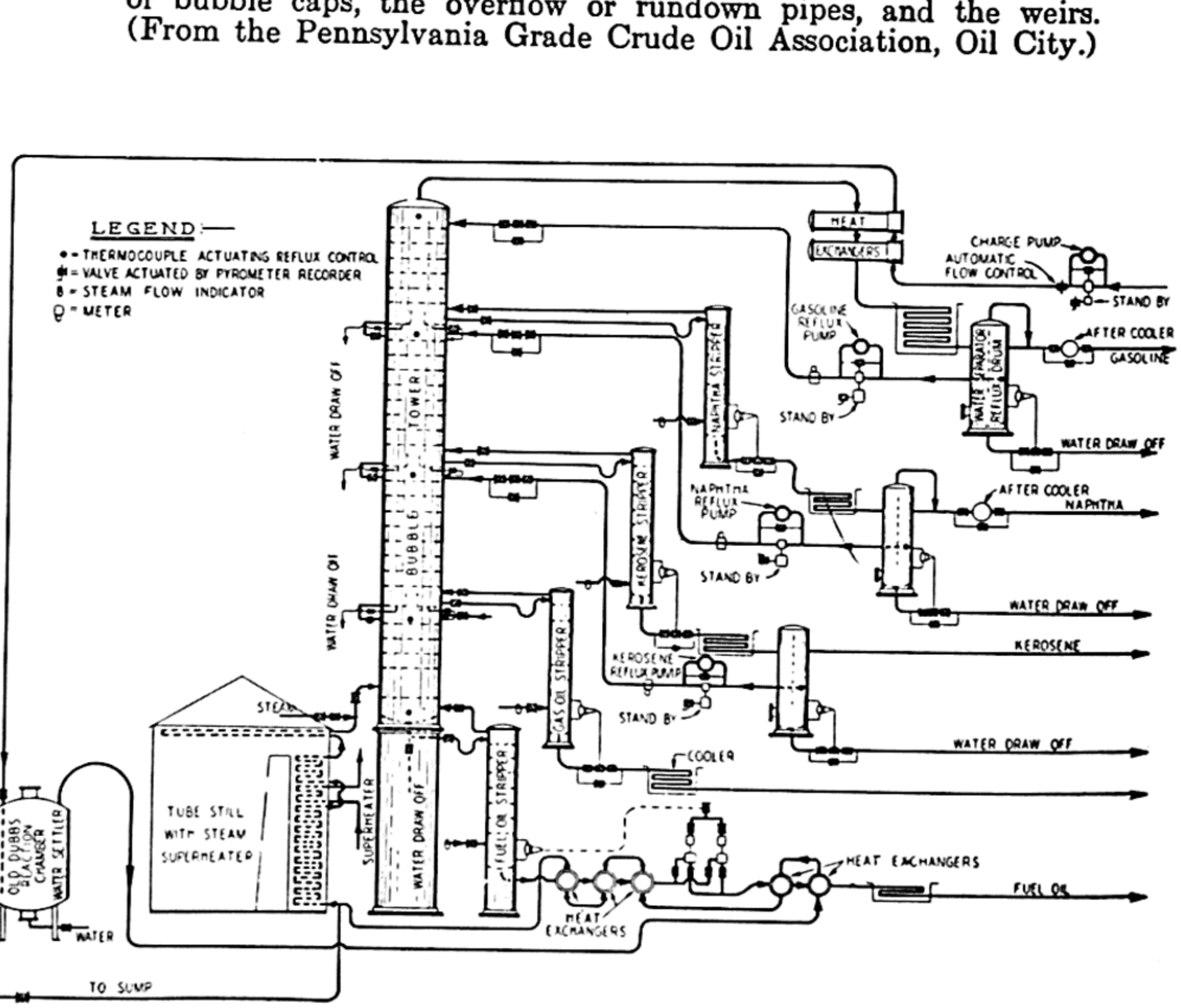


FIGURE 198.—Diagrammatic flow sheet for a 7000 barrel Tulsa unit, showing tube still, bubble tower, four auxiliary plate towers used as strippers, with condensers, after coolers, three reflux pumps, and heat exchangers. (Courtesy of National Petroleum News.)

efficiency upon the number of plates, the construction of caps, baffles across the deck (so that the liquid must take a long path before it reaches the next overflow pipe), deck space, reflux procedure, and velocity of vapors.

Continuous Distillation-Skimming Unit. The method of working is well illustrated by the diagrammatic flow sheet in Figure 198 of a 7000-barrel per day unit of the Producers and Refiners Corporation [21] at Tulsa, Oklahoma. The crude oil picks up heat in the gasoline vapor heat exchangers; then, after passing through a settler for removal of any water, more heat in the fuel oil heat exchangers. At a temperature of 350° F., it now enters the tubes of the furnace, where six oil burners raise its temperature to above 700° F., but below cracking temperature, for this is a skimming unit, that is, a plant for the separation of the gasoline and other fractions just as they

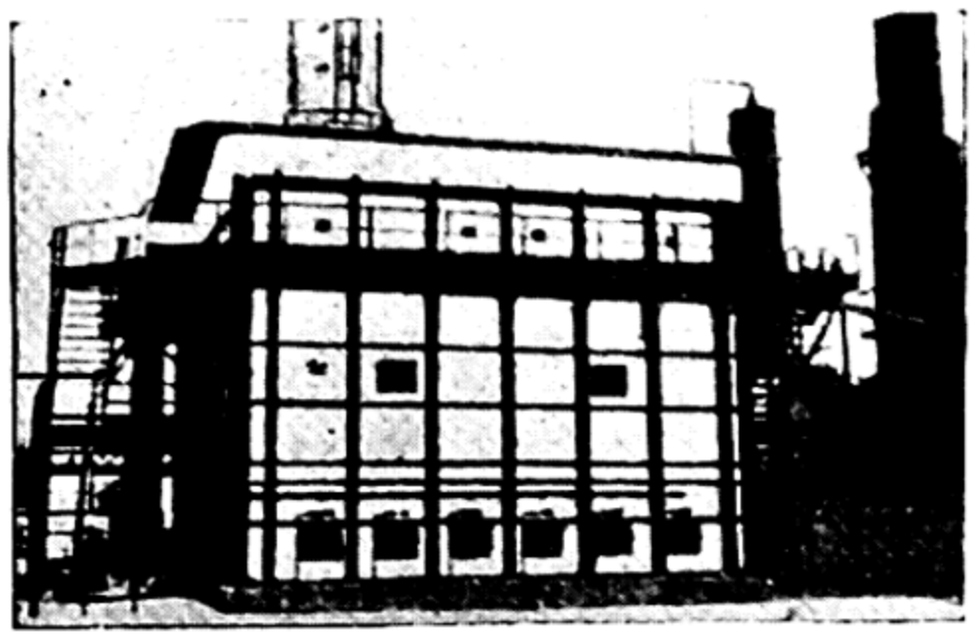


FIGURE 199.—View of the tube still, or oil heater, in the 7000 barrel unit at Tulsa. The bubble tower can just be seen in the center rear of the picture.

are in the crude. The mixture of hot oil and vapors enters the bubble tower, and fractionation takes place. The tower is 10 feet in diameter, and 100 feet high. Gasoline vapors are taken off overhead; a naphtha cut 7 plates below the top; next a kerosine cut; then a gas oil cut; while finally the residual oil forms the fuel oil cut at the bottom of the still. For reflux, there are returned to the still a part of the gasoline, now cold, a part of the naphtha, and a part of the kerosine, both also cold, at the points indicated. The effect of the return of such cooled liquid to the point in the still where material of similar composition is met by it, is essentially to retard the vaporization of the more volatile of the constituents. Each fraction is cleared of any admixed higher boiling fraction in a small auxiliary plate tower, the stripper, which receives superheated steam. (*See* Fig. 198.) For the kerosine, for example, the stripper returns overhead to the still a mixture of gasoline, naphtha and water vapors. Condensed water in the bubble tower is released at the points indicated. The fuel consumption, exclusive of the steam, is 1.5 per cent of the throughput. This unit replaces a battery of seven shell stills of the older type.

Three-stage Distillation Unit. The single-stage bubble tower unit for crude oil distillation is supplemented by two- and three-stage units, especially the latter, of which there are several standard designs. In one of these,[22] the first stage works at 25 to 75 lbs/sq in. pressure, flashing off light

[21] "One man operates new 7000 barrel pipe still skimming unit," Allen S. James, *Natl. Petroleum News*, 21, 73, Nov. 27 (1929).

[22] Badger unit, flow sheet and description in Process Handbook, *Petr. Ref.*, 27, part 2, p. 44 (Sept., 1948).

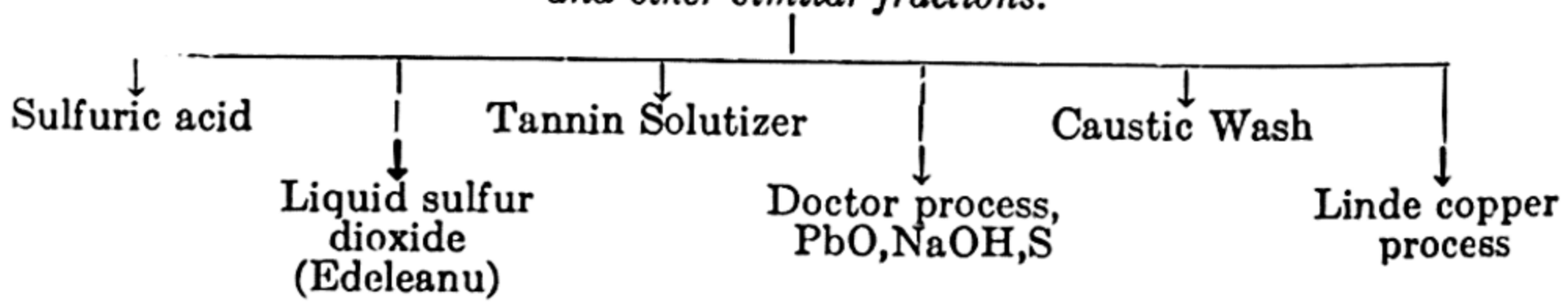
gasoline water and hydrogen sulfide. The residual oil passes to a first oil heater, then to the second stage tower, giving (1) light naphtha overhead, (2) a heavy naphtha, kerosine and gas oil as side streams, and (3) bottoms, which are sent to the second oil heater. All the fractions, including the bottoms, are stripped with steam. From the oil heater, the heavy bottom fraction enters the vacuum tower—which is equipped like the others with plates, condensers, strippers and exchangers—and furnishes a heavy gas oil overhead, light and heavy neutral stock as side streams, and a heavy residuum as a bottom product. The heat in the first stage is from a heat exchanger.

Chemical Purification. The chemical refining of the several products, when necessary, may be done by agitation with 66° Bé. sulfuric acid (generally 3 pounds of acid to each barrel of oil, followed by a water wash, then by a dilute caustic wash). The amounts of sulfuric acid consumed at one time are so great that a plant for recovering the sulfuric acid from the "sludge acid" is a part of many refineries. In more recent years, other methods have to some extent displaced the sulfuric acid wash.

A modern method of purification which saves the by-products without injuring them is the Edeleanu process. It employs liquid sulfur dioxide, which is introduced near the top of a tower completely filled with the liquids; the well cooled distillate (gasoline, naphtha, kerosine, or a lube fraction) enters near the bottom; both are in spray form. The droplets of the oil fraction must rise through the body of the liquid sulfur dioxide; the droplets of the fresh solvent must sink through the layer of hydrocarbons. Two layers continue to form, the sulfur dioxide being the lower one (sp gr 1.45 at 68° F.). There is continual removal of the liquids to make room for the incoming material. The asphaltenes, carbogens and sulfur-containing impurities dissolve in the sulfur dioxide, and flow out with it. In a separate vessel, the sulfur dioxide is vaporized, re-compressed and re-cycled, leaving the extract which, depending upon the nature of oil, may have commercial value. The upper layer dissolves a small amount of sulfur dioxide, which is driven off by gentle heat in a separate still, and saved for re-use; a refined product ready for the market is obtained. The Edeleanu process continues in service in its original form and in a number of modifications for which the original invention furnished the inspiration. A few processes for purifying a naphtha and kindred fractions are shown in Table 86. A table of 13 processes will be found in the literature.[23]

The caustic wash has been gaining over the doctor treatment in the last few years. The fraction is scrubbed with 5 per cent NaOH to remove H_2S;

TABLE 86.—*Processes for the chemical purification of naphtha, gasoline, kerosine, and other similar fractions.*

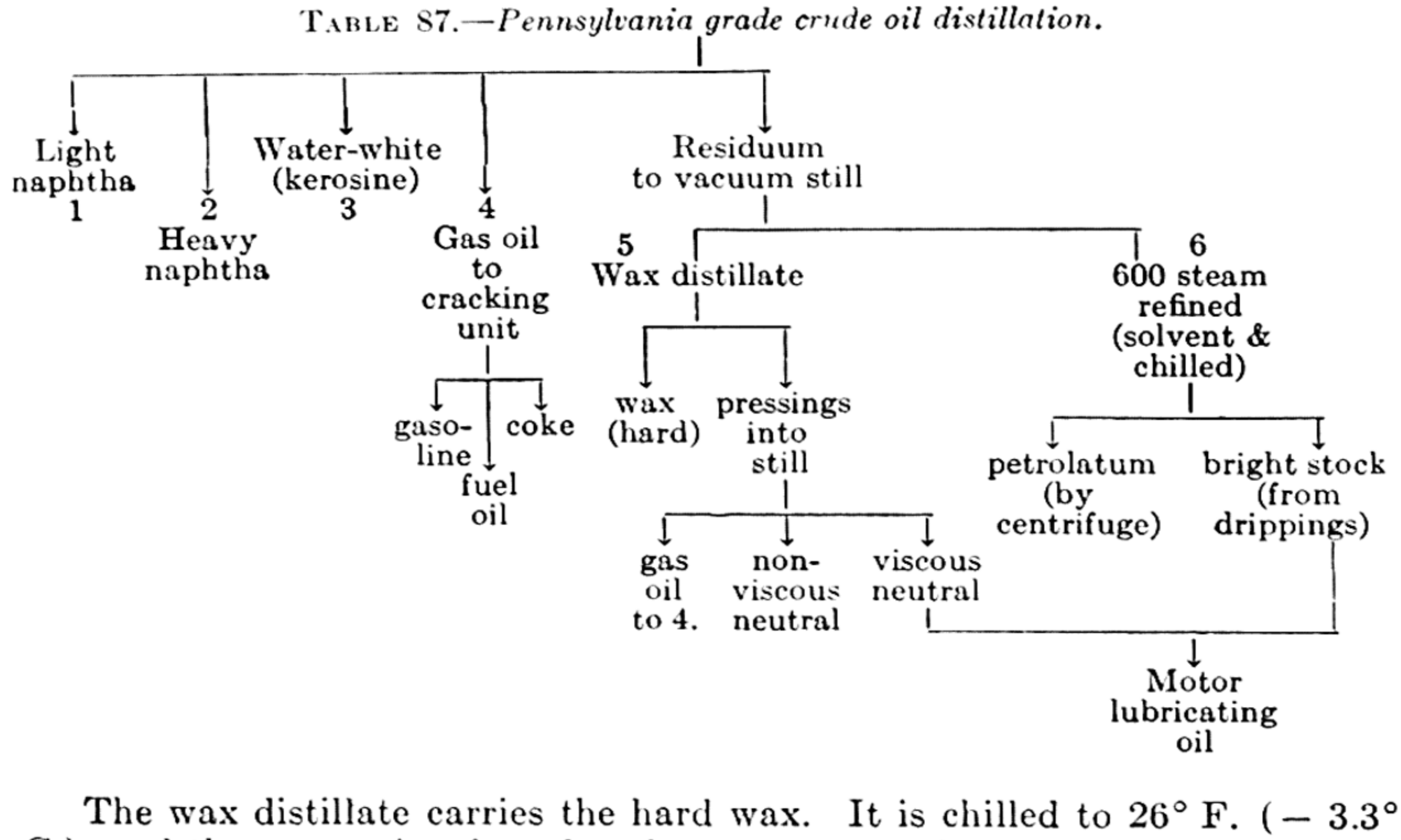


[23] *Petr. Ref.*, 21, 407 (1942), repeated in 25, 510 (1946).

then with 20 per cent NaOH to remove mercaptans (R-SH). The mixing is done by turbomixers, by contactors, or by bubbling the fractions through the caustic solution in vertical towers.

Cylinder Stock and Wax Distillate. Many crudes give distillates in the following order: light naphtha, heavy naphtha, water-white, gas oil, fuel oil, then wax distillate, indicated in Figure 198, and the residuum, in certain cases the most valuable product. The Pennsylvania grade crudes, which are always class A, leave a residue so low in suspended carbon and so free from asphaltic impurities that it forms an article of commerce under the name of "cylinder stock."[24] It is refined in a vacuum column still with steam injection, giving a "pressable wax distillate" overhead, and "600 steam refined" [that is, heated to 600° F. (315° C.)] as a bottom product, not volatilized; this latter is diluted with naphtha, filtered, chilled, and its suspended soft wax separated in a centrifuge, giving petrolatum. The clear solution is passed through a still to drive off the naphtha; it may be bleached by passing it through granular clay, and there results "bright stock" with viscosity, for example, of 145 seconds at 210° F. It is well to note that Pennsylvania grade bright stock is not vaporized, hence has never been subjected to the extreme heat necessary for vaporization.

TABLE 87.—*Pennsylvania grade crude oil distillation.*



The wax distillate carries the hard wax. It is chilled to 26° F. (− 3.3° C.), and the suspension forced under a pressure of 300 pounds into a filter press set in a room which is kept cold. The press may be, for example,

[24] Example of cylinder stock:

Penn stock, viscosity	100–125	sec. at 210° F.
	1600	sec. at 100° F.
Coastal stock, viscosity	125–130	sec. at 210° F.
	3060	sec. at 100° F.

In early 1949, the quotations for cylinder stock in tank car lots ranged from 33 to 38 cents per gallon.

36 feet long, with 350 circular cast iron plates, 5 feet in diameter. The filter cloth is cotton duck; the press has central feed. Once a day the press is opened and the wax removed; as it still contains 40 per cent oil, it is "sweated," that is, warmed in shallow pans with false bottom on which the wax rests, while the oil flows into collecting troughs. The wax left in the pans, now free from oil, is melted and run through bauxite in cylinders 2 feet wide and 20 feet high, to remove the color. The white wax is cast into blocks for shipment, or is made into candles. In addition, it is used in laundries, for waxed papers and drinking cups, and for a variety of household purposes.[25]

The oil filtrate from the wax press passes to a still, with steam injection, to give a gas oil, a non-viscous neutral oil, and as residue, a viscous neutral oil. The latter is filtered through granular clay, and becomes the finished viscous neutral, with viscosity of 180 at 100° F.

Lubricating oils for the market are then produced by blending viscous neutral and bright stock in various proportions.

The value of cylinder stock is reflected in the price per barrel for Pennsylvania grade crude, which was $3.55 (Bradford) and $3.34 (S. W. Pa.), while Oklahoma was $1.58, Panhandle $1.60, West Texas $1.37, and the average, $1.41 (1946). The higher value is one reason also why it is worth while in Pennsylvania to flood the oil sand with water to recover the residual crude.

Processes for Increasing the Amount of Available Gasoline. With the rapid growth of the motor-car industry, the petroleum product which became the most sought after was gasoline. Soon the straight-run gasoline no longer sufficed in quantity, and methods for obtaining more gasoline were actively sought. Motor gasoline may be obtained as shown below.

Motor gasoline including aviation gasoline are obtained by

Straight distillation of crude oil	Cracking gas oil or fuel oil from petroleum crude	Polymerization of C_3 and C_4 hydrocarbon gases	Natural gasoline from wet natural gas	Synthetic liquid fuels

Cracking Processes. On distilling crude oil, there is obtained a large percentage of middle oil, including gas oil, light fuel oil, and heavy fuel oil, for which, until the last few years, there was very little demand. By heating gas oil in an oil heater, similar to the one shown on page 497, and allowing it to expand in a fractionating tower, it was found that a high percentage of lower-boiling components were formed, which were in fact gasoline. The decomposition of an oil during its distillation is a common and generally unwelcome occurrence of the organic laboratory. The large molecule is sensitive to heat; it breaks down into smaller fragments, some of which

[25] An interesting 29-page pamphlet on "Candle manufacture, with special reference to tropical climates," by Professor N. N. Godbole, has recently been published; it depicts the teaching of the making of candles in India, and the materials available, with their properties and costs. Benares Hindu University, Benares, India, 1935.

reunite, or unite in new ways. The cracking art makes skillful use of this defect, and guides the breakdown to produce a maximum of the desired gasoline. Cracking produces a variety of products: gases, low- and medium-boiling naphthas, suitable for gasoline and kerosine, gas oil and fuel oil fractions, residual oil and carbon, depending partly on the kind of stock fed to the unit, and partly upon temperature, pressure and design of the equipment.

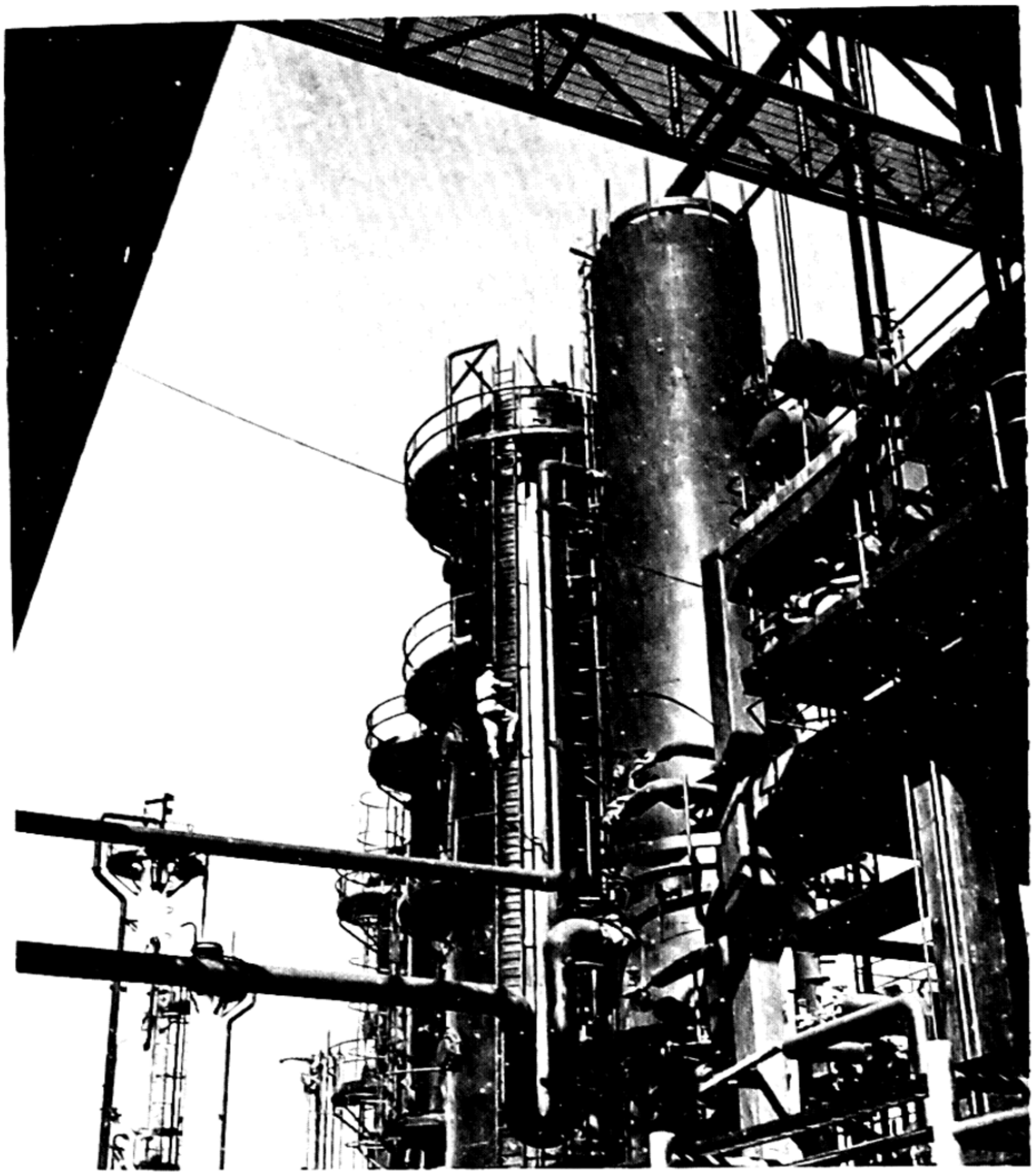


FIGURE 199a.—Charging, cracking and refining equipment in Continental Oil Company's refinery in Wichita Falls, Tex.

Thermal Cracking. In the early years of the cracking art, a flowing stream of gas oil, for example, was exposed for a period of time in steel tubes to high heat under a moderate pressure. It was then released to a large chamber at lower pressure, wherein gases, vapors and liquid could separate. The condensed vapors and the liquid were then separated by fractionation in the usual way. The oil could also be vaporized first, and then subjected to the heat of cracking. A large number of processes were

developed and operated successfully; the most common was the so-called "tube and tank" process. Thermal cracking is still practiced, especially in smaller refineries; in most of the larger refineries, as well as in a number of the smaller ones, thermal cracking has been displaced by catalytic cracking, which is really thermal cracking in the presence of a catalyst.

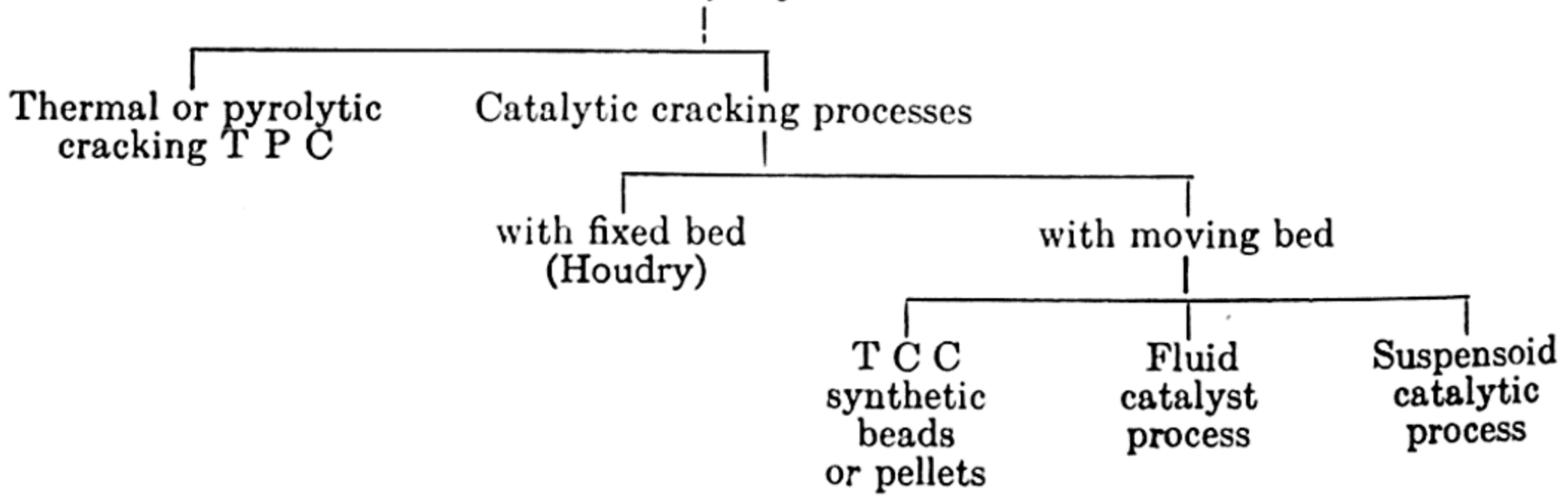
Advanced forms of thermal cracking in newly designed or adapted units are in favor today. One type purposely seeks propylene and butylenes, the production of which was formerly considered a defect; they are of value now because they can be polymerized to give a high octane fraction suitable for blending into gasolines. Other types provide reforming of the oil as well as cracking; still another, described below, furnishes large amounts of ethylene.

In the Thermofor Pyrolytic Cracking (TPC) process,[26] non-catalytic pebbles, heated in an upper chamber, drop by gravity into a reactor where they meet (countercurrently) the oil vapors introduced as liquid feed. Cracking takes place, and the product leaving the reactor is quenched at once, to prevent the decomposition of the ethylene. Charging an East Texas crude, 38.4° A.P.I., there are produced 22.3 per cent by weight of ethylene, 12.2 per cent of propylene, 14.1 per cent methane, 37.2 per cent of liquid product. The pebbles are preheated to 1515° F.

The more conventional Donnelly Cracking Process [27] has for its essential parts multiple heating elements including a viscosity breaker; a vapor separator; and a bubble tower, which produces two liquid fractions, each of which is delivered to its own separate cracking coil for further treatment, and is then returned to the separator and bubble tower. Gas and gasoline pass out overhead. Residuum is withdrawn from the separator to storage. A mid-continent reduced crude (a crude from which gasoline and kerosine fractions have been removed), 25° A.P.I., cracked by the thermal process, gave 53.5 per cent by volume of gasoline, testing 69-70 on the octane scale, and 37.5 per cent fuel oil of 7° A.P.I.

Catalytic Cracking. In the late thirties, the higher compression in gasoline motors demanded fuels with better antiknock properties, higher octane ratings, and higher lead susceptibility.[28] It had been established that

TABLE 88.—*Processes for cracking gas oil and other heavier oils to produce naphthas for gasoline.*



[26] *Petr. Ref.*, Process Handbook, Sept., part 2, 72 (1948).
[27] *Petr. Ref.*, Process Handbook 26, 200 (April, 1947).
[28] Antiknock compounds, lead susceptibility, octane rating are described on page 514.

cracking in the presence of a catalyst produced a gasoline with higher octane number than thermal cracking of the same stock. The requirements of the armed forces in the war years for high-octane motor fuel, especially aviation gasoline, stimulated intense activity in the invention and construction of catalytic processes. The first catalytic process was the Houdry, with fixed catalyst beds, which dominated the scene for several years. Other processes with moving beds are now in the ascendency.

In the Houdry process with fixed bed (Figure 200), cracking is performed

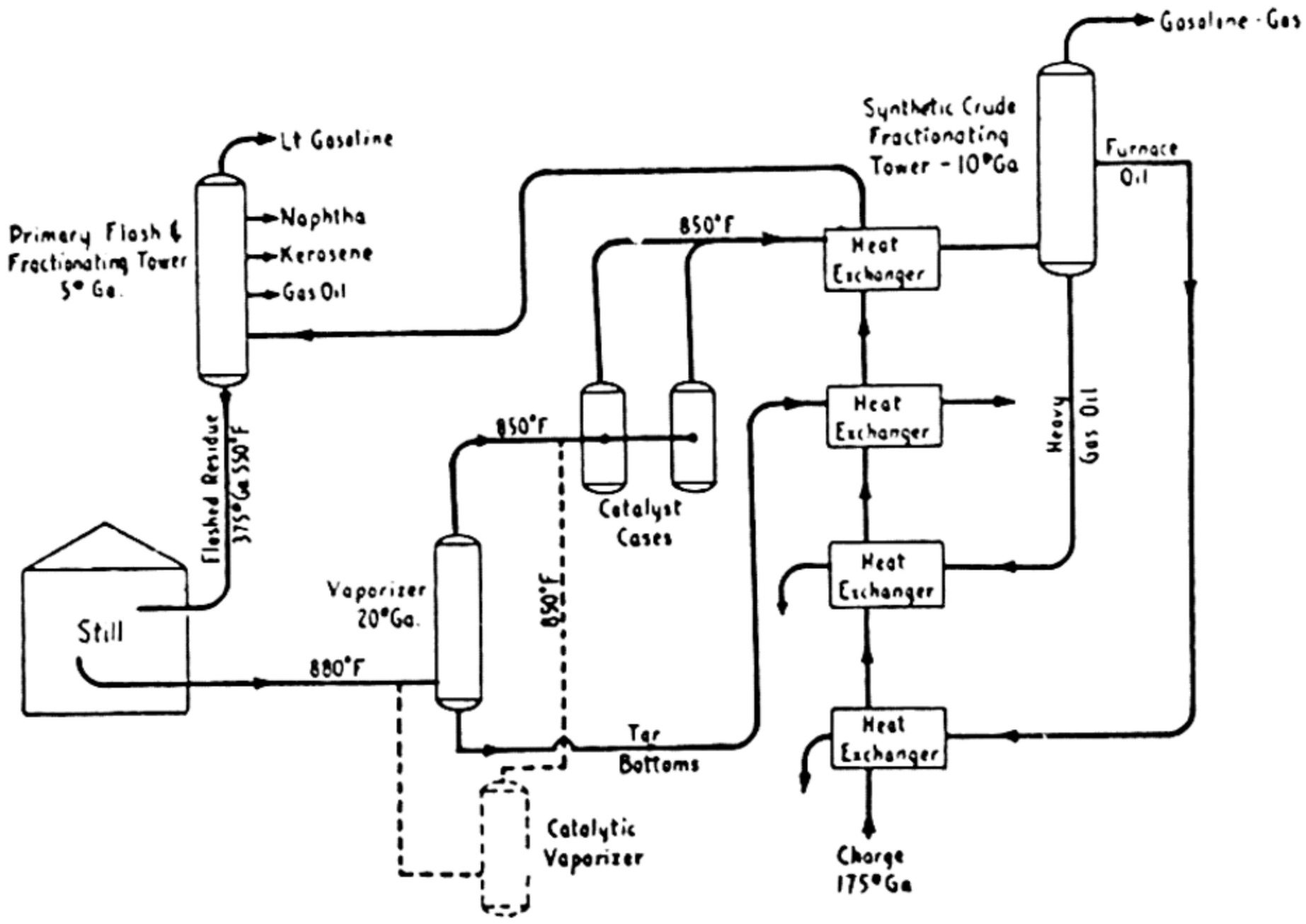


FIGURE 200.—General flow diagram of the Houdry catalytic cracking process, showing crude-topping combined with catalytic cracking. The equipment and connections for burning off the carbon deposit in the catalyst cases is not shown. (From "Catalytic processing by the Houdry process," *Oil and Gas Journal*.)

while the oil vapors are in contact with the solid catalyst (activated hydrosilicate of alumina in molded form,[29] or synthetic alumina-silica beads). The charge of crude, after a preliminary distillation for naphtha, kerosine and gas oil, passes to an oil heater, and then to the vaporizer, working at 20 lb./sq. in. pressure. The vapors, at 850° F. (454° C.), enter the catalyst case, react, and then leave overhead. After passing a heat exchanger, they are partly liquid, partly gas; thus they reach the synthetic crude fractionating tower, where they are separated into gasoline and gas overhead, furnace oil as a side stream, and a heavy gas oil as bottoms. As cracking progresses, the catalyst becomes fouled by deposited carbon, which must be burned off. This is done by a stream of heated air after shutting off the oil vapors. Excessive temperatures during combustion are prevented by cir-

[29] "Catalytic processing by the Houdry process," by Eugene Houdry, Wilber F. Burt, A. E. Pew, Jr., and W. A. Peters, Jr., *Oil and Gas Journal*, 37, 40–48 (1938).

culating a fused high-temperature salt mixture (a eutectic mixture of KNO_3 and $NaNO_2$) through the inner tubes. By using two, or preferably three catalyst cases, one may be on stream while the other is being revivified and thus the process is made continuous. The heat withdrawn by the fused salt during combustion period is transferred in exchangers to the incoming stock, and to boilers where 450-lb. steam is raised. The cycle in each catalyst case

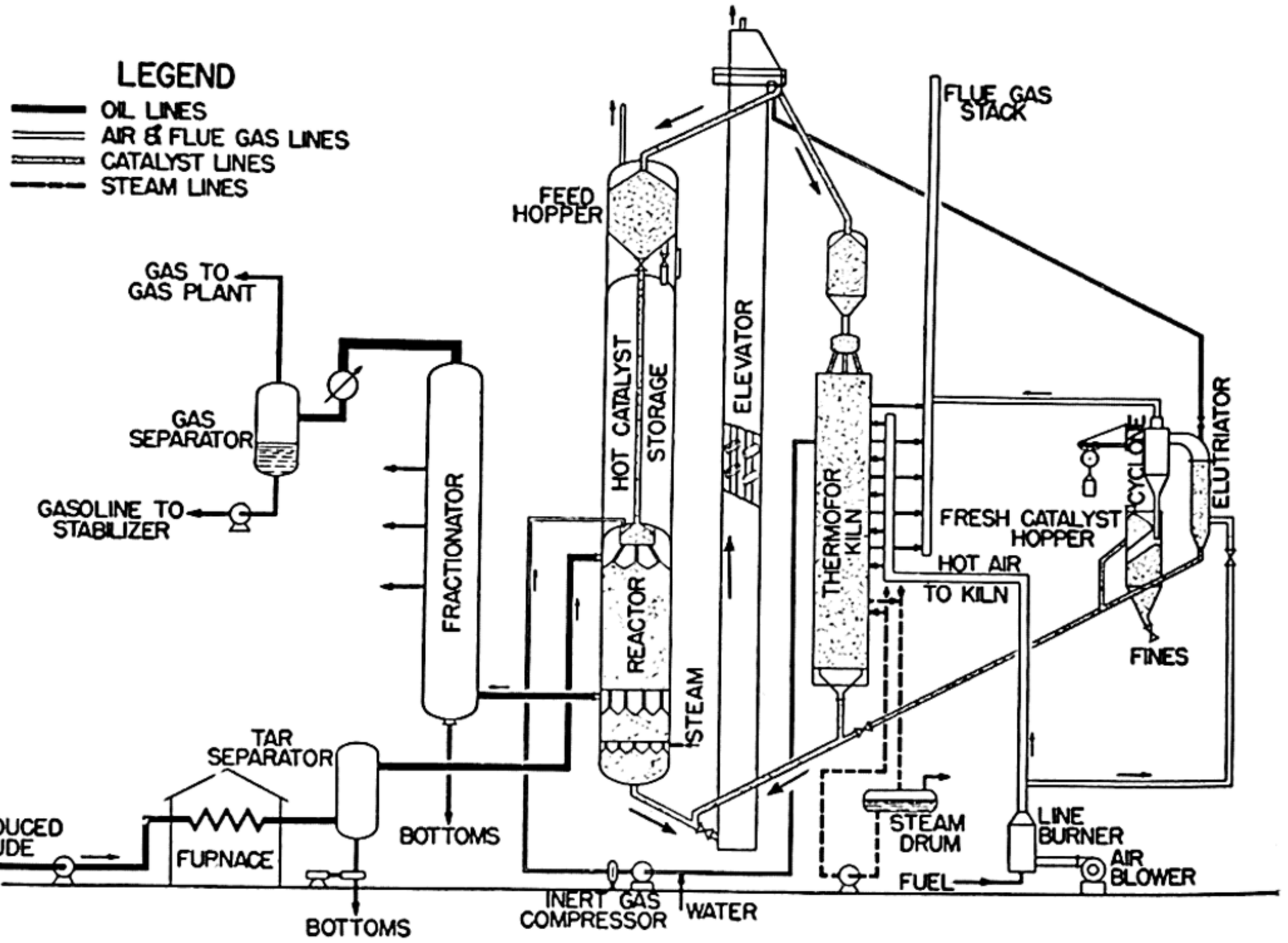


FIGURE 201.—Simplified flow diagram of typical TCC installation; catalytic section. [*Petroleum Refiner*, 25, 238 (1946).]

is 30 minutes: on stream, 10 minutes; purge, 5 minutes; regeneration, 10 minutes; purge 5 minutes.

Thermofor Catalytic Cracking. In Thermofor catalytic cracking, the catalyst is a moving bed (or mass) of small cylinders or spheres of either the clay type or the synthetic type. Of the latter, the best known and most successful are the spherical, slightly opalescent beads of aluminum silicate, averaging $\frac{1}{8}$ inch in diameter. The TCC plant consists of an oil-heating furnace, a reactor, a regenerator, two bucket elevators, a hopper surmounting a vertical standpipe, a fractionating tower, heat exchangers, and auxiliary equipment. The reactor is the chamber in which the vaporized oil comes in contact with the catalyst beads, at a temperature of 900 to 1050° F.; it is here that the cracking of the molecules takes place. The beads bring the necessary heat, and beads and vapors travel concurrently down the reactor. The ratio of catalyst to oil is 1.5 to 3.5, depending upon the nature of the stock. The space velocity varies from 0.2 to 1.0 and over. The cracked gasoline vapors with any unchanged charge leave the reactor

as indicated in Figure 201, and pass to the synthetic crude tray tower, where the gasoline is separated from lighter and heavier fractions.

Some of the vapor is cracked too far, producing carbon which coats the beads, fouling them, and hydrogen, which later passes out as gas. To revivify the catalyst, the beads leaving the base of the reactor are first purged with steam, to remove oil vapors and adsorbed oil,[30] and then drop

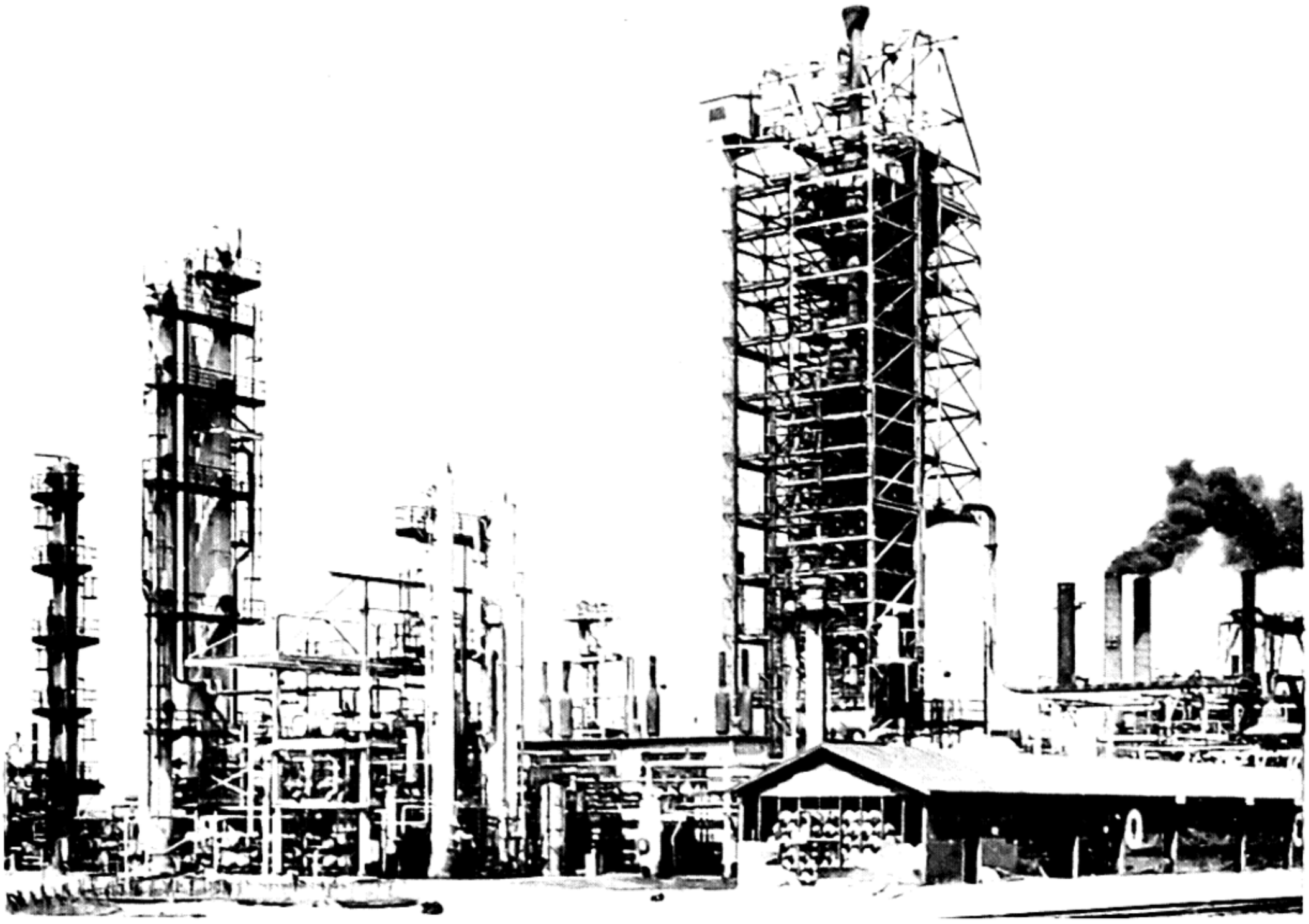


FIGURE 202.—View of a Thermofor catalytic cracking (TCC) unit. The tall structure encloses the kiln (near side) and the reactor (far side). The large upright cylinder adjacent to and to the right of the tall structure is the "synthetic crude" distilling column. The unit fore and to the left of the TCC structure is the gas plant. The three gas plant distilling columns on the extreme left are the deethanizer, depropanizer, and stabilizer (debutanizer), going from left to right. The overhead crane on the extreme right rises over the Houdry unit. Such cranes are symbolic of Houdry units. (Courtesy of Socony-Vacuum Oil Co., New York.)

into the buckets of an elevator which lifts them to the top of the regenerator or kiln, in which the accumulated carbon-rich deposit is partially removed (it decreases from 4 to 0.2 weight per cent) by burning it off. The kiln is of square cross-section, and has a 6-inch lining of insulation.

Excessive heat (over 1200° F.) must be avoided, as it destroys the activity of the catalyst (which is what the carbon deposit also does). For this reason the kiln is divided into, for example, 10 zones.[31] Each zone

[30] *Trans. Am. Inst. Chem. Eng.*, 41, 229 (1945).
[31] *Pet. Ref.*, 26, 555 (1947).

receives a supply of combustion air; part of the deposit is burned away, and the hot beads are cooled at once by passing them down coils containing water, which is changed into steam. Each zone has two outlets for the fire gases and excess air. The lower zones are taller, allowing more time in the burning space; this is done because the last portions of the deposit burn off more slowly. The residence time is 5 to 10 minutes for the upper zones, and 20 minutes for the bottom or clean-up zone. The revivified beads enter the boot of the elevator, which lifts them to the reactor feed hopper, whence they travel down a vertical standpipe of sufficient length to overcome the pressure in the reactor, which may be from 5 to 15 lb/sq in. A top seal of flue gas, entering at the base of the leg, is provided to prevent the escape of the oil vapors. The major part of the seal passes up the leg and out to the atmosphere; a small part enters the reactor.

In a unit with capacity of 13,000 barrels per day, there will be 400 tons of catalyst. The make-up per day is 0.6 ton. In order to prevent an accumulation of fines, part of the catalyst leaving the reactor is cleaned by elutriation. The reactor is a steel cylindrical vessel 16 feet in diameter and 40 feet high. The assembly of reactor, regenerator and elevators resembles a 12-story building; inspections and visits are made by means of a passenger elevator.

Charging a coastal naphthenic gas oil of 28° A.P.I., into the TCC unit, there are produced, for example, 53.9 volume per cent of a motor gasoline testing 53.3° A.P.I., with an octane number of 83 (CFR-M). After adding 3 milliliters of tetraethyl lead (a liquid), the octane number was 90.3 (CFR-M). Tested by the CFR-R method, the ratings were 94.2 and 100, respectively. A catalytic gas oil produced at the same time was 34.0 volume per cent, with density 21.7° A.P.I.

Another example exhibits the difference in results for "once-through" contrasted with recycled distillate fuel oil.

TABLE 89.—*Thermofor catalytic cracking of gas oil boiling over the range 450 to 800° F.*

	Once-through		Distillate fuel oil recycled	
Gasoline	40	volume %	62	volume %
Distillate fuel oil	42	" "	—	" "
Heavy gas oil	5	" "	15	" "
Butanes (1)	7	" "	16	" "
Coke	3	weight "	7	weight "
Gas (2)	7	" "	10	" "
Polymer gasoline from (2) and part of (1)	4	volume "	9	volume "

Once-through is practiced when distillate fuel oil, which is suitable for domestic fuel oil blends, is in demand; for maximum gasoline, recycling is done. The overall yield of liquid products averages about 90 per cent by weight; the difference is carbon and gas.

Akin to the TCC process is the Houdriflow catalytic process.[32] It differs from the TCC in the following features: the pellets or beads are elevated

[32] "Simplicity of process and low investment cost stressed," *Petr. Ref.*, 28, 110 (1949).

by a flue gas lift; the reactor is constructed over the regenerator, now circular, the two forming a single more compact structure; catalyst-to-oil ratios of 4 to 6 are provided, permitting a wider choice of stocks to be processed.

Synthetic Alumina-silica Beads. The synthetic bead catalyst on which the Thermofor catalytic cracking process in part depends is made on a large scale at the rate of 50 tons a day by a process developed under the stress of World War II. Vast amounts of better gasoline—that is, gasoline with

FIGURE 203.—View in the synthetic alumina-silica bead plant, showing 12 forming towers, each with its fluted cone. In the room beyond are the numerous wash and treating tanks. (Courtesy of Socony-Vacuum Oil Co., New York.)

higher octane ratings, and with higher lead susceptibilities—were required for aviation. The demand was met by new plants employing either beads or clay pellets as catalyst, or fluid catalysts, supported by fixed beds (Houdry).

The beads are formed by the reaction of an acidified aluminum sulfate solution of high purity and a sodium silicate solution. The inlets for the two solutions are so arranged that the silicate solution enters in a mantle of aluminum sulfate solution. A sol forms instantly, and is allowed to flow over a fluted cone flaring outward at the base. The sol separates into small streamlets which travel down the grooves of the cone, separating into drops. The latter fall into a tall body of oil in which the drops become essentially spherical, then gel before reaching an underlying water layer. At this stage the bead is ten times the size of the final dehydrated one. The soft beads leave the forming tower flushed by water; they are washed in hot water (to set the shape), in an aluminum sulfate solution (to remove sodium), and in various waters carefully adjusted to remove the alum. The washed beads are dried

by gentle heat to a 10 per cent moisture content, and then are raised to the top of the tempering kiln, where they are dehydrated by falling through the burner pipes (propane) to the bottom, and thence to a box. The drying plant includes 3 dryers, each with 4 conveyor belts 9 feet wide. Vast amounts of especially treated water are required.

The synthetic bead catalyst is intended primarily for oil refineries, but it is sold for application in other processes. By a slight modification, a desiccant bead is produced. The density of the particle is 1.10; surface area, 420 square meters per gram; pore volume, 0.50 cubic centimeter per gram; average pore diameter 47 Å. The individual bead, $\frac{1}{8}$-inch in diameter, will support a 200-pound load; a mass of beads in a column will support a load of about 3000 lbs./sq. in. before crushing.[33]

The Fluid Catalyst Cracking Process. In the fluid catalyst cracking process, the heated oil vapors pick up a fine powdered clay, or a synthetic catalyst in powder form and the two whirl about in intimate contact in the reactor, where the cracking of the oil molecules takes place. The catalyst is said to be *fluidized*, for the mixture of powder and vapors behaves in many respects as if it were a single fluid. The density of the fluid may be varied by altering the ratio of catalyst powder to vapor. The cracked vapor enters an internal cyclone where most of its dust is released and returned to the reactor, while the comparatively clean vapor travels to a slurry settler, then to a fractionator which condenses, in rotation, heavy gas oil, light gas oil, and raw gasoline or naphtha; gases pass from a final cooler to a recovery system.

The catalyst becomes fouled, and must be reactivated. To this end, a portion of the fluidized catalyst is bled constantly from the reactor, separated from its accompanying vapors (which return to the reactor) in the "spent catalyst stripper," and travels downward to a stream of combustion air which carries it (upward) into the regenerator, where the carbon-rich deposit is burned off. The flue gases travel through an internal cyclone, depositing their dust, to a steam-producing heat exchanger, to an electrical precipitator, where the last of the powder is caught, and thence into the atmosphere. The recovered catalyst, now clean, reenters the regenerator, is joined there by make-up catalyst, and the two together, at a temperature of 1100° F., are ready to enter the reactor. On the way there, they meet the incoming preheated oil feed, or charge, which they flash-vaporize. The catalyst and vapors in the reactor feed line are forced along and up by the velocity of the entering vapors and by the head of fluid in the regenerator standpipe, and enter the reactor at its lowest point, rising through the bed of fluidized catalyst. The temperature in the reactor is maintained at 900-950° F.; the cracking reaction consumes heat, but the catalyst powders bring in the necessary heat from the regenerator. In this function, the catalyst may be thought of as a heat-transfer agent.

The full-scale unit may have a capacity of 20,000 barrels a day or more. Smaller units are built to handle, for example, 3,300 barrels per day. In the

[33] *Petr. Ref.*, 22, 353 (1943).

full-sized unit, there are several hundred tons of catalyst in circulation. The cleaned catalyst from the regenerator is fed into the reactor at the rate of a box-car a minute, and let it be noted, without moving parts.[34]

The synthetic fluid catalyst is a plural gel, forming microspheres, with surface area of 500 square meters per gram of gel. Three different gels are offered, made up as follows:

	Silica-alumina*	Silica-magnesia*	Silica-magnesia-alumina*
SiO_2 (dry basis)	85	67	65
MgO	—	30	30
Al_2O_3	13	0.5	3
Apparent density at 1000° F.	0.6	0.8	0.6

* Courtesy The Davison Chemical Corporation, Baltimore, Md.

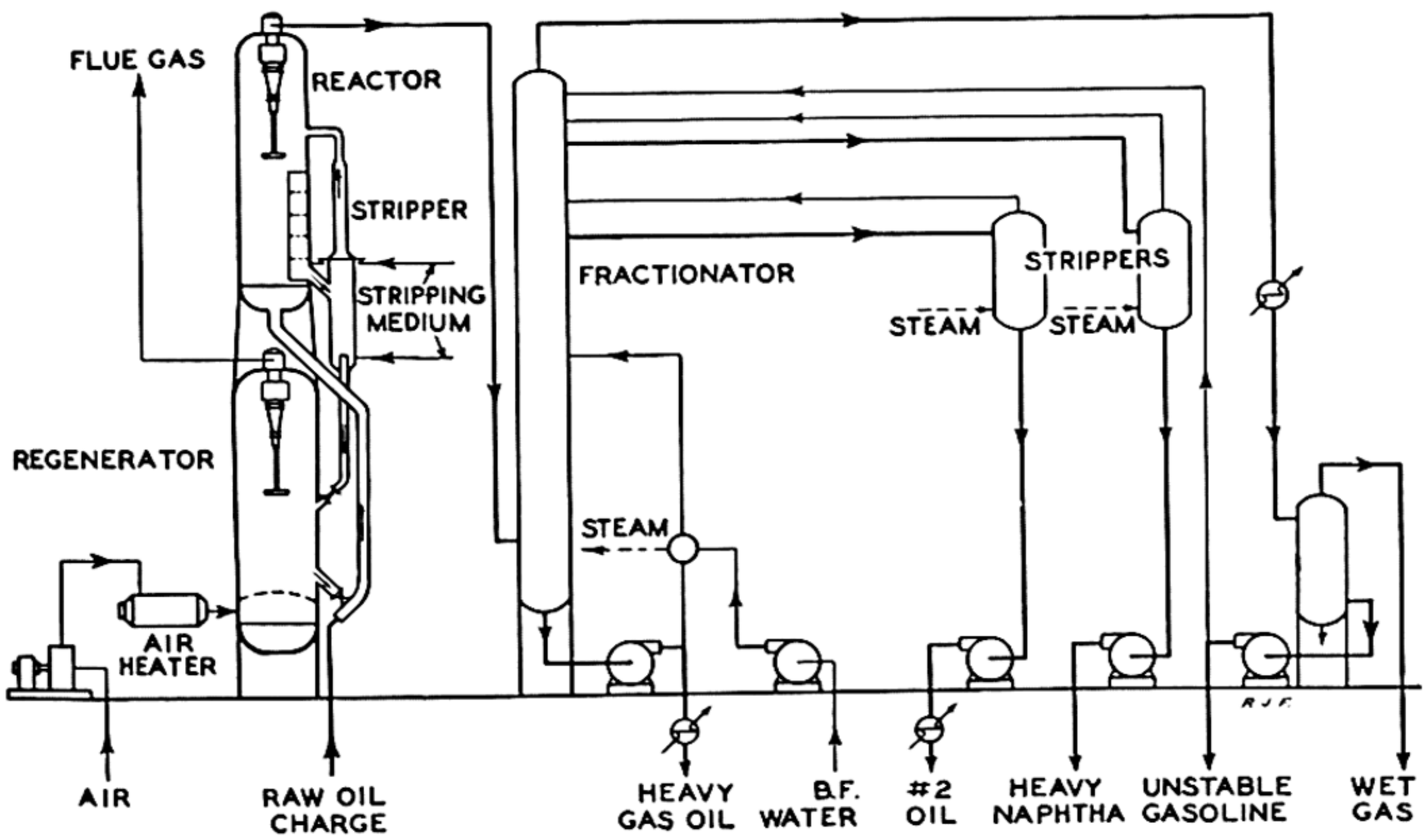


FIGURE 204.—The fluid catalytic process for cracking petroleum oil fractions. (Based on a sketch in the process book of Lummus Company, New York, N. Y.)

As already mentioned, the cracked vapors from the reactor enter the fractionator, in the bottom of which the slurry of heavier oils and residual catalyst is formed. If desired, the slurry oils may be recycled and returned to the reactor.

In Figure 204 a fluid catalyst plant is shown in which the reactor surmounts the regenerator, forming a single structure.

There are over 40 fluid catalyst cracking plants in petroleum refineries in the United States; not only has the fluid catalyst principle proved itself in this industry, but it has been adapted to other industries, notably in synthetic liquid fuel installations.

[34] "Fluid Progress," an illustrated booklet published by the M. W. Kellogg Company, 225 Broadway, New York 7, N. Y.

Natural Gasoline

Natural gasoline is the liquid which accompanies "wet" natural gas in many regions; it is removed by compression, or by absorption, mainly in straw oil, or by a combination of both processes. The gasoline values are mainly low-boiling, and correspond to hexanes, heptanes, with some octanes and pentanes. Intermediate hydrocarbons may also be separated, although

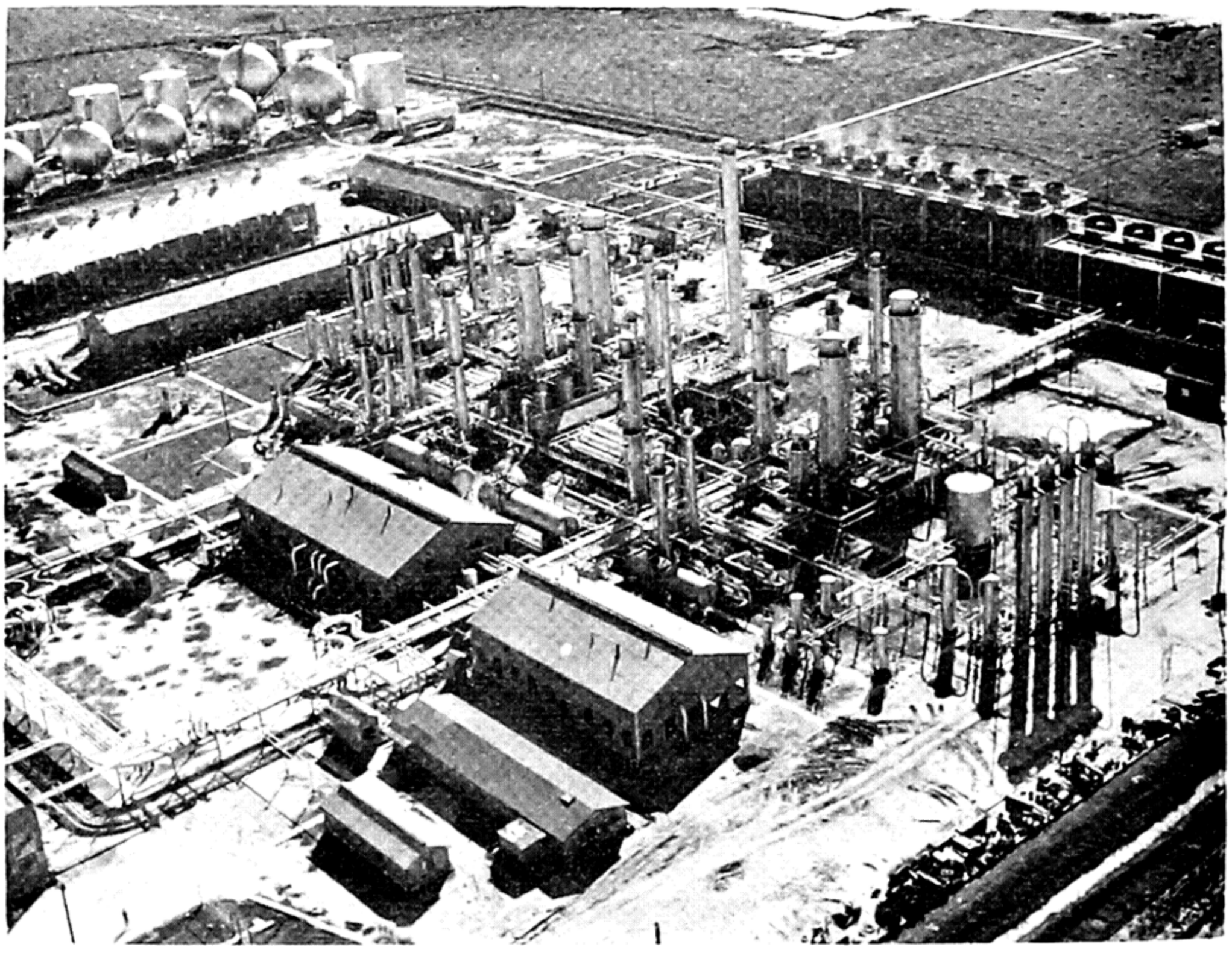


FIGURE 205.—An aerial view of a natural gas processing plant, the Katy Gas Plant, for recovering natural gasoline and other volatile products, by the absorption system. The two oil absorbers are in center right. (Photo by Elwood M. Payne, Houston, Texas.)

less completely, in the form of liquefied petroleum gases (L.P.G.) such as propanes and butanes. The relative amounts are reflected by the figures for the daily production in one plant in the south treating 30 million cubic feet of gas daily, drawn from 670 wells: propane 360 barrels; isobutane 190; normal butane 210; isopentane 108, and debutanized gasoline 547 barrels. In this typical plant, the wet gas, compressed to 700 lbs./sq. in. gauge, enters two 40-plate towers operated in parallel, where it meets the absorber oil which enters at the top and travels down, leaving the tower as saturated absorber oil. Unabsorbed gas leaves overhead; in part, it serves a fuel gas in the plant; the balance is compressed and returned to the field. The "fat" oil is first flashed to a pressure of 385 lbs./sq. in., to release most of the absorbed methane and ethane with some propane and higher components.

By means of a reabsorber, such values in propane and higher hydrocarbons are in large part recovered. The flashed oil passes to a primary or high-pressure still, where again the lower hydrocarbons are driven out and saved for other purposes. The oil then passes to the low-pressure or main still where the gasoline components, all of which may be compressed to a liquid at practically atmospheric pressure, are removed and collected. The stripped lean oil is cooled and returned to the absorbers.

In 1945, there were 568 natural gasoline plants, of which 181 operated by compression, and 387 by absorption; of the former, 52 were in West Virginia, and of the latter, 116 in Texas. There were 38 cycling plants, of which 31 were in Texas. To clarify the terms used: A natural gasoline plant may be defined as a light hydrocarbon processing plant which obtains its feed in vapor form. The feed vapor may be casinghead gas from oil-well separators, or it may be from gas wells, or from both. A "cycling plant" usually has a feed stock from high-pressure wells in the range of 1500 to 5000 lbs./sq. in. and higher. The gasoline values are extracted in high-pressure absorbers, working at 2000 lbs./sq. in., for example. The tail gas is recompressed to 4000 lbs./sq. in., and returned to the producing formation through an injection well. Yields vary from 0.5 gallon to 5 gallons per 1000 cubic feet of gas treated.[35]

The production of natural gasoline in 1946 was 2,750,318,000 gallons, and of L.P.G. 1,400,877,000 gallons. Other products bring the total to 4,836,412,000 gallons for the natural gasoline industry.

TABLE 90.—*Production of motor fuel in the United States (1946).**

	Barrels
Refinery gasoline	
Cracked	390,208,000
Straight-run	302,347,000
Natural gasoline	112,004,000
less liquid petroleum gas sales	26,719,000
Benzol	2,070,000
Total production	776,054,000
Daily average	2,126,000

* "Minerals Yearbook," 1946.

Improving Gasolines by Additions and Reactions

Gasolines can be improved by the addition of foreign substances, by forming the hydrocarbon molecule in a definite manner, and by rearranging the molecular structure of the existing molecule, with or without simultaneous removal of hydrogen. The following processes alter the structure of the molecule, or add to its size, thus raising its octane rating:

Stabilizing	Alkylating	Hydrogenating
Reforming	Hydrofining	Polyforming
Isomerizing	Hydroforming	

Other companion processes which have definite aims but which also improve the octane rating are the isomate process in which for instance *n*-butane in the liquid state is isomerized to isobutane, with anhydrous hydrogen chloride

[35] "Minerals Yearbook," 1946.

as a catalyst; cyclization, and aromatization. The improving process is applied to a selected type and grade. Among the additions, the most important is tetraethyl lead.

Antiknock Compounds. In order to prevent the familiar knock in an internal combustion motor such as in automobiles, when hot and laboring, and the loss of power which occurs as a result, a number of substances may be added to the fuel with success. The effectiveness per unit weight of these substances varies greatly. The best known antiknock compound is tetraethyl lead, $Pb(C_2H_5)_4$, a liquid which is also the most efficient, for 0.04 per cent of tetraethyl lead will retard the detonation as much as does 25 per cent of benzene. Tetraethyl lead is made by the action of ethyl chloride on a lead-sodium alloy of definite composition, in the presence of a small amount of ethylene bromide.

The antiknock composition compound is a mixture of 3 parts by volume of tetraethyl lead, a liquid, with 2 parts ethylene bromide; this mixture is added to the gasoline, with a small amount of bromonaphthalene, and a red dye (*see* Chapter 28), and the treated gasoline is then retailed. The ethylene bromide is added in order to change the lead oxide formed during the combustion to the volatile lead bromide which passes out with the exhaust gases. The use of gasoline containing tetraethyl lead allows the use of high-compression motors and thus increases the power efficiency of the fuel. It is to tetraethyl lead that the manufacturer of aviation gasoline looks for reaching the high octane rating required.

There are many other substances which have antiknock properties, for example aromatic compounds, branched-chain paraffins and unsaturated hydrocarbons. The catalytic cracking processes furnish a gasoline which is superior in two respects: it has a high octane rating itself, and it responds to small additions of tetraethyl lead, by testing considerably higher in octane value after the addition; in other words, it has a high "lead susceptibility." It should be noted in passing that purifying a gasoline by chemical means is a good way to raise the lead susceptibility. Because tetraethyl lead is poisonous, both the substance itself and the gasoline made from it must be handled with proper precautions.[36]

Iron carbonyl is used in Europe as an antiknock additive; it is effective, but the spark plugs must be freed from magnetic oxide at frequent intervals.

Octane Number. The octane number is the rating of a gasoline as to its antiknock properties on the basis of a standard sample consisting of "iso-octane" and normal heptane mixed in various proportions. The older standard was a benzene addition. Normal heptane tends to knock, while "iso-octane," which stands for 2-2-4-trimethylpentane, has marked antiknock tendencies. By mixing the two in all proportions, a series of fuels is obtained which covers the whole scale of possible gasoline mixtures; such a series is exact, and reproducible. It is used as primary standard; selected gasolines are compared with them and then serve as working standards, because they are cheaper. A gasoline has octane number 70 if on compressing it in a standard engine, it begins to knock with the same compres-

[36] Public Health Bull., No. 148, Washington, D. C., 1925.

sion ratio which causes a mixture of 70 parts "iso-octane" and 30 parts *n*-heptane to develop a knock in the same engine under the same conditions.

The density and boiling points of "iso-octane" and *n*-heptane are almost identical, an advantage for this purpose.

The octane rating is determined by two methods which generally give different results. One is the CRF-M method (the "motor method"), which usually gives lower figures; the other is the CFR-R method (the "research" method). For high values, such as 100, both methods frequently agree.

100-Octane Fuel for Aircraft. Iso-octane itself is not an aircraft fuel. The 100-octane aircraft fuel is a blend, and is usually prepared by mixing

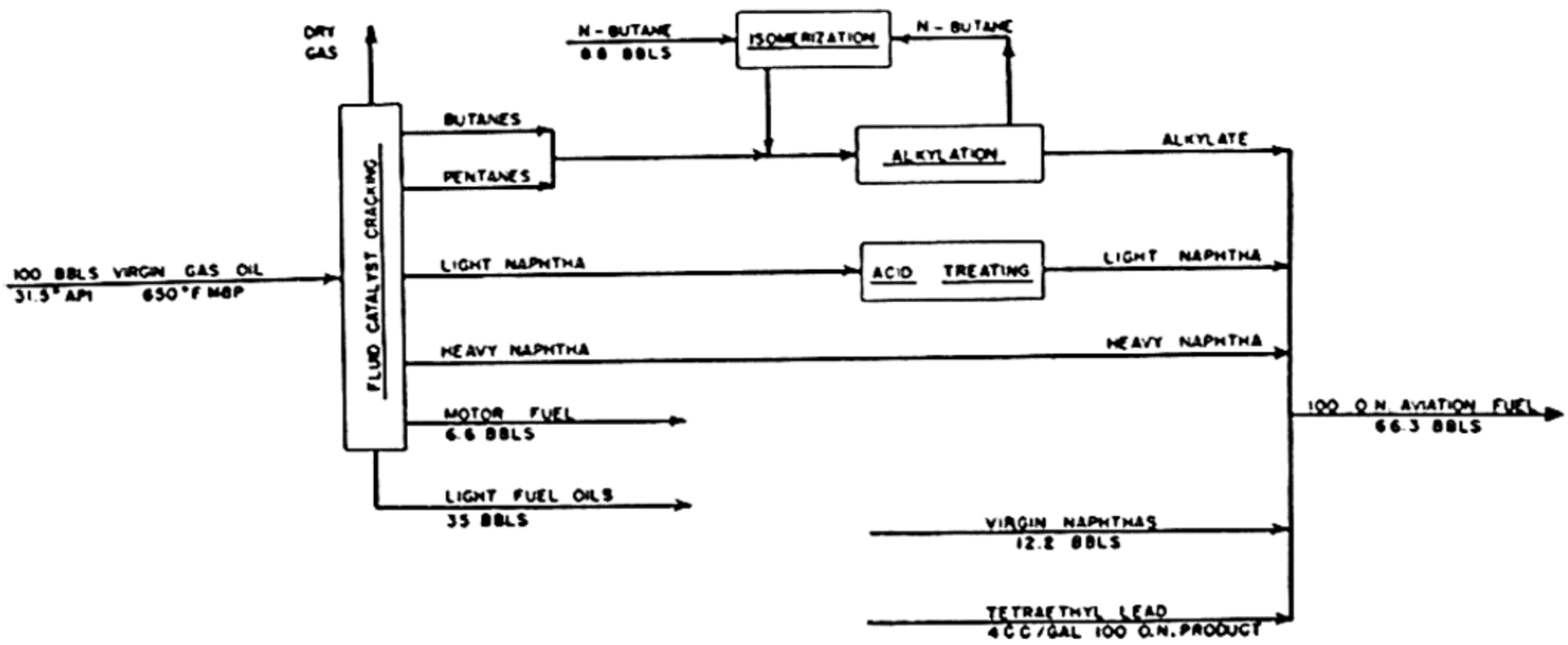


FIGURE 206.—Aircraft fuel (or aviation fuel) made by catalytic cracking, starting with virgin gas oil. [*Petr. Ref.*, 22, 362 (1943).]

commercial iso-octane, a selected straight-run gasoline designated as aviation gasoline, isopentane, a very volatile hydrocarbon, and enough tetraethyl lead to reach 100 octane in antiknock rating. An example follows:

40 per cent of 95-octane iso-octane
45 per cent 74-octane aviation gasoline
15 per cent isopentane
3 cu. cm. tetraethyl lead

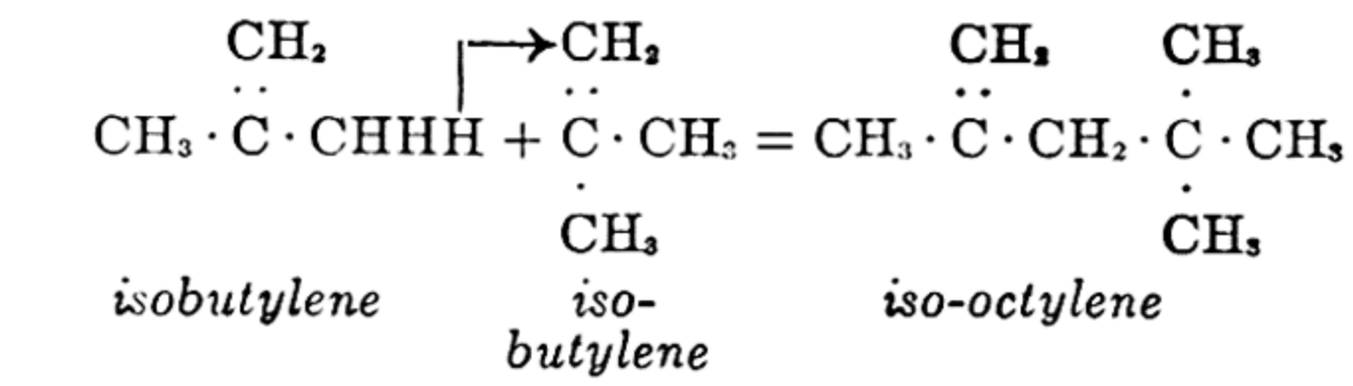
The gravity of the blend is 69.6° A. P. I., the initial boiling point 100° F. (37.78° C.), the end boiling point 249° F. (120.56° C.), before addition of the lead. The octane rating is 98 (CFR-M), or 100 (CFR-R). The isopentane supplies the volatility at the lower temperatures which the iso-octane lacks. The term "aviation gasoline" as used here indicates the gasoline which becomes the base of the aircraft fuel.

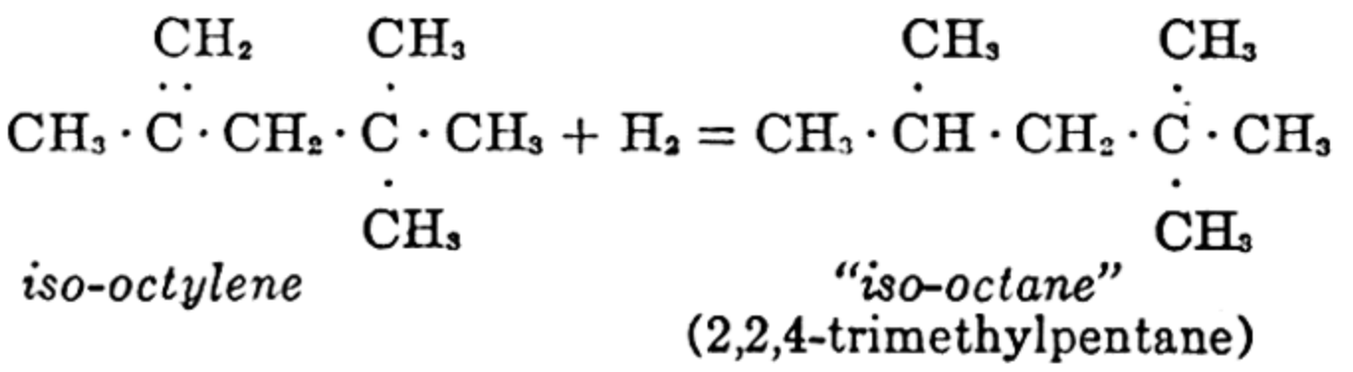
An aircraft fuel made entirely from gas oil by catalytic cracking, supplemented by alkylation preceded by isomerization, is shown in Figure 206.

To illustrate the advantage of high-octane fuel: an airplane which requires 8 minutes to climb to a height of 13,000 feet with 87-octane fuel, will climb to the same height in 5.6 minutes with 100-octane fuel.

Making Pure Iso-octane. One way to prepare the chemical substance iso-octane, more exactly designated as 2,2,4-trimethylpentane, is to dimerize

isobutene, and then hydrogenate the resulting octylene. A charging stock rich in isobutene is selected and sent to the catalyst chamber maintained at 260° to 325° F. (127 to 163° C.) under a pressure of 700 pounds; the product is debutanized and distilled to furnish the iso-octylene fraction. The latter is converted to iso-octane by low-pressure catalytic hydrogenation with a nickel catalyst; pressure 75 pounds, temperature 325° F. (163° C.), U. O. P. process. A charging stock less rich in isobutene may be used. The reactions are as follows:





Isobutylene may be dimerized in the cold, by the catalytic action of sulfuric acid, from an impure mixture of this gas with other refinery gases; the octylene produced may then be isolated as before, and converted into iso-octane by catalytic hydrogenation. In charging stock in which normal butylene as well as isobutylene is present, one molecule of normal butylene may be condensed with one molecule of isobutylene to form a different octylene, which after hydrogenation gives a branched-chain octane. It has been found that such a product is nearly as good in antiknock property as iso-octane itself, and it is likely that it will be produced in increasing quantities.

Alkylation. The alkylation process for the production of high-octane gasoline is the result of the discovery that paraffin hydrocarbons in the presence of a catalyst unite with olefins. The "alkylate" produced from a properly selected stock is 91 to 95 in octane number, and boils within the limits of aviation gasoline, 40 to 150° C. (104 to 302° F.). The reaction may be illustrated by isobutane, which unites with ethylene to form neohexane (2,2-dimethylbutane). Two methods are available, the thermal method, and the catalytic method at low temperature. The alkylation conditions in the thermal method are 510° C. (950° F.) and 5000 lbs./sq. in. pressure; the high pressure is required to repress the cracking tendency resulting from the high temperature. The olefin concentration is kept so low with relation to isobutane, such as 1 to 10, that its polymerization is suppressed. Neohexane itself has an octane rating of 94, and is very susceptible to tetraethyl lead additions; its volatility makes it a desirable blending agent with other fractions for aviation gasoline.

In the catalytic method for alkylation the isoparaffins and olefins meet in the presence of 96 to 100 per cent sulfuric acid, at temperatures between 0 and 10° C. Again by using the proper stock there may be produced

essentially 2,2,4- or 2,2,3-trimethylpentanes; or fractions containing these hydrocarbons in a high percentage may be obtained in a distillation subsequent to the alkylation.

The alkylation reaction has largely supplanted the iso-octane process, for it doubles the yield and eliminates the hydrogenation process.

The improvement in the octane rating is shown in the following figures [37]:

	Charge	Product
Gravity	51.4° A.P.I.	51.3° A.P.I.
Octane number (A.S.T.M.)	47.2	77.0
Reid vapor pressure	0.4	8.2
Initial boiling point	222° F.	99° F.
Boiling point 10%	250	174
Boiling point 50%	292	270
Boiling point 90%	367	339
Maximum boiling point	436	368

The latest catalyst for alkylation is anhydrous hydrogen fluoride, a liquid which is not miscible with hydrocarbons.[38] The two liquids are brought into intimate contact in a contactor, such as the one shown in Figure 207.

The importance of alkylation diminished with the decrease in the demand for aircraft fuel once the war was over. The decreased demand is reflected in the decrease in the production of aircraft fuel.

TABLE 90a.—*Production of aircraft fuel (complete aviation gasoline).*

Aircraft fuel,	1944	1945	1946
100 octane and over	136,130,000	124,215,000	5,342,000 barrels
Other grades	60,253,000	28,180,000	20,070,000 barrels

Hydroforming Petroleum Naphthas. A new process for "reforming" hydrocarbons, and converting low-octane gasolines to high octane was placed in successful large-scale operation about ten years ago.[39] It is a high temperature, catalytic process, and the action takes place in the presence of hydrogen; yet hydroforming is not hydrogenation; on the contrary it is dehydrogenation, and part of the hydrogen so produced is recirculated merely to control the rate and extent of the dehydrogenation. The catalyst is molybdena on alumina. The most important property of the catalyst is that which causes ring formation and permits ring preservation in molecules which have just undergone partial dehydrogenation (aromatization). The final product thus contains a high percentage of aromatic, and a small quantity of aliphatic hydrocarbons, compared with the feed. The product is unusually stable and may be blended directly with finished gasoline, after gas removal, in a separator followed by distillation in a stabilizing tower.

It is well to have two catalytic reactors so that while one is functioning, the other may be freed of the small amount of coke deposited on the surface of the catalyst granules. The coke is burned off with caution, so as not to harm the catalyst; this is accomplished by adding controlled amounts

[37] *Chem. Met. Eng.*, 48, April, p. 77 (1941).

[38] "The development of the hydrogen fluoride alkylation process," C. G. Gerhold, J. O. Iverson, H. J. Nebeck, R. J. Newman, *Tr. Am. Inst. Chem. Eng.*, 39, 793 (1943).

[39] "Hydroforming, a new refining process," D. J. Smith and L. W. Moore, *Chem. Met. Eng.*, 48, 77 (1941). Flow sheet in "Process Handbook," *Petr. Ref.*, Sept., part 2, p. 112, (1948).

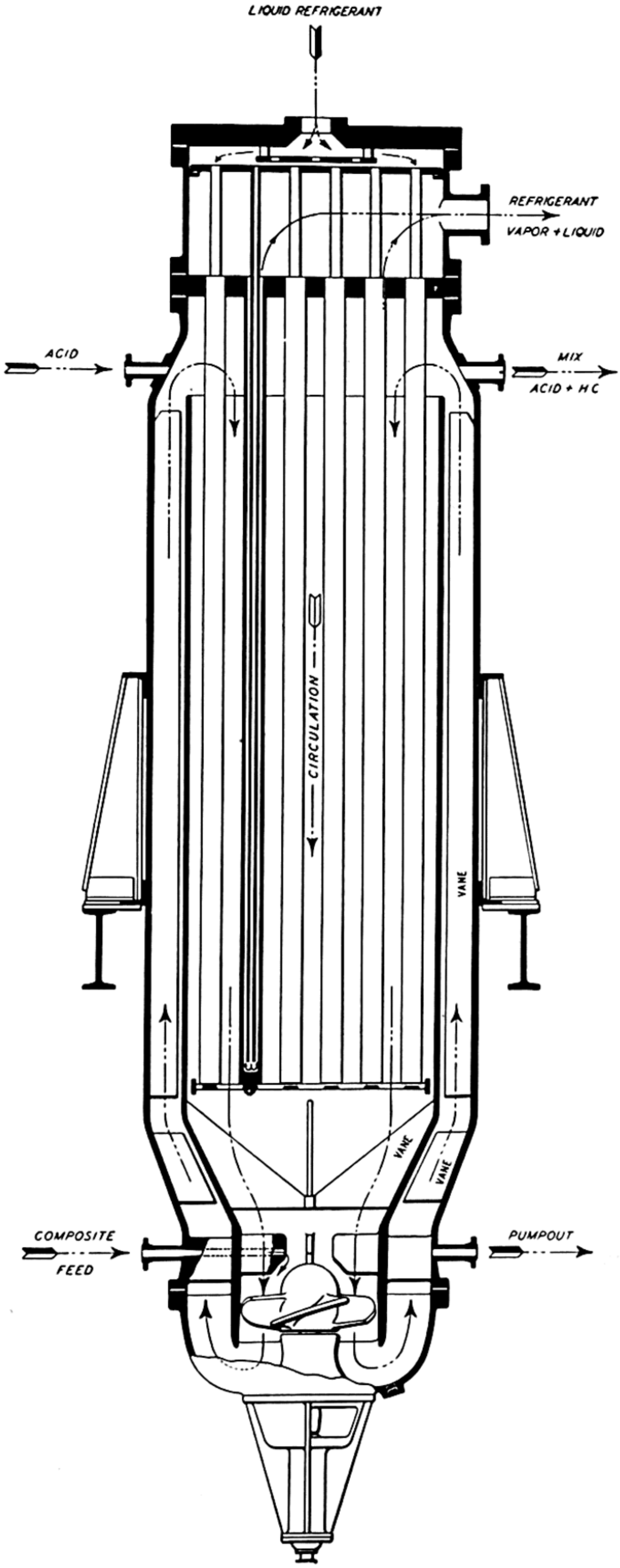


FIGURE 207.—Vertical cross-sectional view of the cylindrical Stratco alkylation contactor. The liquid hydrocarbons enter at lower left, just over the propeller. Liquid hydrogen fluoride enters near upper left and travels down the spaces between the cooling tubes to the propeller where the two immiscible liquids are emulsified. The emulsion travels upward through the annular space along the outer wall, then down again to the propeller. After reaction, the mixed hydrocarbon and acid leave near upper right. Refrigerant or cooling water enters at top of contactor, travels down, then up the cooling fingers and out at upper right. (Courtesy of Stratford Engineering Corporation, Kansas City, Mo.)

of air to an inert flue gas. For any given octane level, coke deposition is a function of the amount of recycle gas and its hydrogen concentration. The removal of the coke restores to the catalyst its original activity. The plant at Texas City can reform 7,500 barrels per day of heavy naphthas rating 40 or so octane into a product of 80 octane (A.S.T.M.) with a yield of 80 per cent.

Low-octane naphtha side-streams taken from the crude topping system are so enriched by the process of hydroforming that they contain 40 to 50 per cent of aromatic hydrocarbons, of which 15 to 20 per cent is toluene. The removal of the toluene from accompanying hydrocarbons in the same boiling range (200-240° F.) is performed by azeotropic distillation. Methyl ethyl ketone-water, the best azeotrope-former for this purpose [40] is added to the naphtha, and the mixture introduced into a fractionating still. The azeotrope-former (M E K-water) passes out overhead, carrying with it the non-toluene hydrocarbons. The bottoms in the still consist of 99+ per cent toluene. The process is continuous. The importance of toluene is now much less than in the war period. The production from all sources in 1946 was 33,499,000 gallons; from July 1, 1944, to June 30, 1945, the allocations were 249,910,000 gallons, also from all sources, but mainly from petroleum.

Polymer Gasoline. The polymerization of olefin-bearing gases has as its main object the production of high-octane motor fuel. An almost ideal charging stock is the gas formed in vapor-phase cracking operations. In one catalytic polymerization process, the catalyst is copper-pyro-phosphate.[41] The heated vapors, mainly C_3 and C_4 hydrocarbons at 300 to 400° F., enter the reactor held at a pressure of about 900 lbs/sq in.

Another solid catalyst which has been mentioned is solid phosphoric acid.[42] The earlier processes were chiefly thermal.[43] A number of thermal polymerization units continue in service, in part because it converts saturated as well as unsaturated C_3 and C_4 (and other) hydrocarbons, whereas the catalytic process acts only on propylene and butylenes.

Kerosine, Fuel Oil, Bunker Oil.

The production of kerosine, also called range oil, light distillate oil including Diesel oil, and residual fuel oil including bunker oil was as follows:

TABLE 91.—*Production of heating and lubricating oils, and wax (1946).**

	Barrels
Kerosine	104,385,000
Distillate fuel oil	287,896,000
Residual fuel oil	469,492,000
Lubricating oil	45,645,000
Wax	840,840,000 pounds average price 4.94 cents/lb.

* "Minerals Yearbook."

[40] "Recovery of toluene from petroleum by azeotropic fractionation," George R. Lake, *Tr. Am. Inst. Chem. Eng.*, 41, 327 (1945).

[41] "Process Handbook," *Petr. Ref.*, Sept. 1942, part 2, p. 128; also p. 124.

[42] "Polymer gasoline," G. Egloff, *Ind. Eng. Chem.*, 28, 1461 (1936).

[43] "The thermal process for polymerizing olefin-bearing gases," M. B. Cooke, H. R. Swanson, and C. R. Wagner, *Petrol. Inst., Los Angeles meeting* (1935). Also, "New Gulf polymerization unit in Port Arthur, Texas, plant," by Ernest Cotton, *Oil and Gas J.*, 37, 25 (1939).

The distillate fuel oil item includes home heating oil and Diesel oil; the latter are selected oils which must meet rigid requirements, among others a specific cetane number. The proportion of Diesel in the total figure above may be estimated as 35 per cent. The price varies; the average for Diesel for shore plants, New York Harbor, for the year 1946 was 6.20 cents per gallon.

Cetane Rating. For Diesel oils, a system of rating analogous to octane rating for gasoline has been established. The best Diesel fuel is the straight-chain paraffin, normal cetane, $C_{16}H_{34}$; the worst is α-methyl naphthalene, just the opposite from the gasoline fuels. Mixtures of these two substances serve as standards, and the cetane number is the percentage of cetane in a mixture with α-methyl naphthalene which gives the same ignition performance (measured in direct ignition lag) as the fuel tested. For heavy fuels, a cetane number of 30 gives a good performance, while for the lighter Diesel engines, a lighter fuel testing 40 to 60 cetane is chosen. The best Diesel fuel comes from a gas oil cut from a Class A or B crude.

The residual fuel oils are thick, black oils, used in heavy industries, by ships and railway locomotives. Bunker oil [44] is a residual oil; bunker "C" for ships was $1.69 per barrel in New York, an average over the year 1946. Crude white scale wax was 4.94 cents a pound.

A process to "stabilize" bunker oil, so that it will not develop sediments in transit and in storage, is the Goodwin process, which consists of "chemical and mechanical treatment of the residuum leading to two materials of value, a stabilized fuel oil, merchantable as Bunker A, B, and C, and a high B.t.u. value residuum suitable as a refinery fuel or a briquette binder." [45]

Hydrogenation. Of the several hydrogenation processes, hydroforming is the high-pressure catalytic one which is applicable to gasolines, Diesel fuel, kerosine and lubricating oil, transforming them from low-quality cuts to materials of superior grades.[46] Taking the last as an example, poor quality lubricating distillates are changed by catalytic high-pressure hydrogenation, or hydroforming, into high viscosity index lubricating oils. The charging stock is pumped into the reactor which contains the catalyst, molybdena on alumina in 1-inch cubes, with hydrogen, all under a pressure of 3000 lbs/sq in. The temperature is close to 800° F. (427° C.). The reaction requires but a short time, and is exothermic. During the reaction, the molecule is rearranged into its most stable form (stabilization) and combined with hydrogen, while at the same time the elements oxygen, nitrogen and sulfur form their corresponding hydrides and leave the oil molecule (purification). Unused hydrogen is recovered, and the liquid product is fractionated. No coke is formed during the reaction.

[44] Two samples of bunker oil

	Sample 1	Sample 2
A.P.I. gravity	15.9	19.9
Saybolt viscosity at 100° F.	207	155
Flash (open cup)	225° F.	200° F.
A.S.T.M. Pour (max. for 115° F.)	50	45
A.S.T.M. Pour (min. for 220° F.)	−10	−20

[45] Dr. T. R. Goodwin, *Nat. Petroleum News*, 21, (2) (May 15, 1929).

[46] "Process Handbook," *Petr. Ref.*, 27, part 2, p. 116, Sept. 1948.

The lubricant obtained has the five qualities required of a perfect lubricating oil: (1) high viscosity index; (2) low pour point; (3) resistance to oxidation; (4) negligible carbon formation; (5) long life. The paraffin-base untreated lubricating oils have (1), (3), and (5); the naphthenic-base lubricating oils possess (2) and (4). By pour point is meant the temperature just below which the oil is too thick to pour.

A mild, simple and economical hydrogenation pressure serves, for example, for the hydrogenation of iso-octene to iso-octane, using as catalyst nickel on a porcelain carrier.[47]

Viscosity Index. The viscosity index [48] of an oil evaluates it with respect to its viscosity-temperature behavior. Any oil becomes less viscous as its temperature is raised. A high viscosity index means that this decrease is moderate, no more than should be expected. A low viscosity index means that an oil thins rapidly, so that at elevated temperatures it is like water, and of no value as a lubricant.

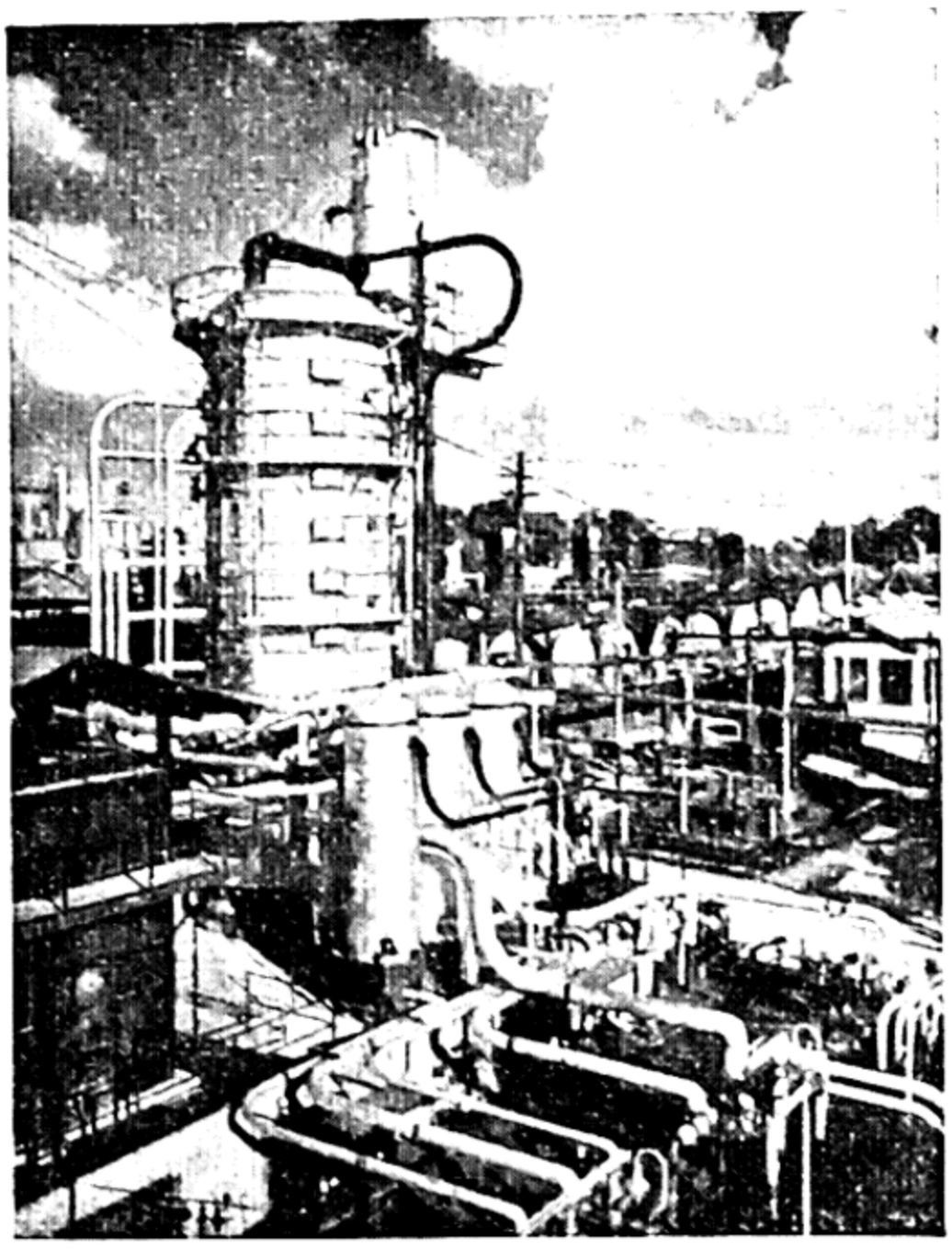


FIGURE 208.—A vacuum distillation tower, which receives the lubricating stock and separates it into several "cuts," preparatory to propane and solvent refining; with its three stripping vessels at its base. (Union Oil Bulletin.)

Solvent Purification of Lube Fractions. The application of liquid sulfur dioxide to the solvent purification of petroleum fractions has been described. There are in addition over 10 processes which purify one or several such fractions, either by dissolving and removing the valuable portion, leaving the less desirable one behind, or by dissolving the impurity, leaving the pure material behind. Solvents are liquid sulfur dioxide, liquid sulfur dioxide with 25 per cent benzene, liquid propane, phenol, "Chlorex," β-β'-dichlor-

[47] *Ibid.*, p. 120.

[48] "Viscosity variations of oils with temperature," E. W. Dean and G. H. B. Davis, *Chem. Met. Eng.*, 36, 618 (1929); "Alignment chart for estimation of viscosity index of oils," I. Laird Newell, *Ind. Eng. Chem.*, 23, 843 (1931).

ethyl ether, $CH_2Cl \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2Cl$.[49] One advantage of liquid propane is that it is obtainable in the refinery itself; another is that in order to remove it, so that the good oil it carries may be collected, reduction in pressure brings about volatilization. This second advantage is shared by liquid sulfur dioxide, which is a solvent for the impurity, the residuum.

In the Duo-Sol process,[50] two solvents operate in a series of 9 pressure vessels and travel in opposite directions. At 8, propane, one of the solvents, loaded with paraffins and parathenes, leaves the system to deliver the purified lubricant; fresh cresylic acid (25 per cent cresylic acid with 25 per cent primary phenol), the second solvent, enters at 8 and travels to 7, 6, until it reaches 1 where it leaves, laden with asphaltenes and carbogens. The fraction to be treated (thus a 23° A. P. I. residual oil from an Oklahoma crude) enters at 3. Fresh propane enters at 1. The propane layer (raffinate) with paraffins and parathenes moves by pressure differential. The extract layer is moved by centrifugal pumps. Vessel number 9 is used as a settler.

Two examples of solvent purification are as follows:

	Motor Oil, Propane-Refined, SAE-30		Motor Oil, Chlorex-refined, SAE-20	
	Duo Sol. (Max B. Miller)			
	Before	After	Without Treatment	With Chlorex treatment
Gravity	25.7° A.P.I.	29.2° A.P.I.	28.4° A.P.I.	31.1° A.P.I.
Pour point	5° F.	5° F.	5° F.	0° F.
Flash point	420° F.	440° F.	430° F.	420° F.
Fire point	480° F.	500° F.	485° F.	470° F.
Viscosity at 100° F.	590 sec.	552 sec.	380 sec.	298
Viscosity at 130° F.	250	250	177	152
Viscosity at 210° F.	65.5	67	57.5	55
Color A.S.T.M.	5½	5 Lt.	6	5.5
Neutralization number	.03	0	.02	0
Carbon Residue	.76%	.18	.6%	.3%
Viscosity Index number	85	100	100	117
S.O.S. % Sludge				
Days 1	0	0	..	0
2	.2	0	..	0
3	1.0	0	1.0	0
4	..	0	..	0
5	..	0	3.5	0
6	..	0	..	0
7	..	0	8.5	0

Lubricants

Lubricating oils now in use are mainly mineral oils refined as described in this chapter; formerly castor, lard, coconut, olive, and many other oils were used without additions. Blends of mineral and fatty oils, vegetable or animal, are used to a considerable extent, particularly in cutting oils in the machine shop. Soluble cutting oils are emulsified with water, and cool as well as lubricate; they contain sulfonated oil with mineral oil.

The thickest oil obtained from the paraffin crude fraction may serve for steam cylinder oil, usually blended with fatty oils. Lubricating agents of still higher viscosity are the greases—calcium or sodium soap jellies emulsified with much mineral oil, and usually containing a little water. To make the calcium soap grease, tallow is pumped (melted) into a steam-jacketed kettle, and hydrated lime added. After the reaction, warm mineral

[49] "A review of the commercial applications of 'Chlorex,'" by W. H. Bahlke, A. B. Brown, F. F. Diwoky, *Oil and Gas J.*, 32, Nos. 3, 60, 62, 72 (1933). See also, "A solvent dewaxing plant," *Chem. Met. Eng.*, 48, 106 (1941), an inset flow sheet.

[50] *Compare* "Refining lubricating oils by solvent extraction," J. V. Hightower, *Chem. Met. Eng.*, 42, 82 (1935); and "The Duo-Sol process," Max B. Miller, *Ibid.*, 285.

oil is run in and mixed. The product is run to cans and barrels while warm and liquid. The final grease contains 10 to 25 per cent calcium soap, 1 to 3 per cent water, and the balance mineral oil. A sodium jelly base is preferred when heat from the outside may reach the lubricated parts.

Wagon axle grease and railroad curve grease are made by the cold reaction of rosin oil and hydrated lime previously suspended in mineral oil. The hard locomotive cup grease, which must be turned down with a wrench, is made by mixing tallow and oil and pouring in a concentrated solution of caustic soda. The reaction takes place in the cold;[51] the mass sets to a solid.

Asphalt, Tar and Road Oil.

The production of petroleum asphalt, road oils and tars as shown below will indicate the importance of the materials. Figures on native asphalts and gilsonite are also given. Petroleum coke has been described in Chapter 17.

TABLE 92.—*Production of asphalts and road oils in the United States (1946).**

Native asphalts	777,457	short tons
Manufactured or petroleum asphalt produced in domestic refineries†	8,165,600	short tons
Road oil	6,175,000	barrels

* "Minerals Yearbook."
† 20 per cent manufactured from foreign crudes.

Native asphalts are solid bitumens (that is, hydrocarbons) which melt on heating to the temperature of boiling water, or near it. Trinidad Lake asphalt is a solid bitumen found naturally mixed with silica and clay; it occurs in just that form only on the island of Trinidad. Other asphalts are found impregnating amorphous limestone, crystalline limestone, or shales, in Europe (Sicily and other localities), in Oklahoma, Utah, and California. The asphalts are used for paving cements, and for this purpose are frequently softened by the addition of residues from the distillation of various crude oils.

TABLE 93.—*Percentage yields of refined petroleum products in the United States (1946).**

Gasoline	
Cracked	22.5
Straight-run	17.1
Total	39.6
Kerosine	6.0
Distillate fuel oil	16.6
Residual fuel oil	24.9
Lubricating oil	2.7
Wax	.2
Coke	.6
Asphalt	2.6
Road oil	.4
Still gas	5.1
Other	1.3

* "Minerals Yearbook."

[51] "Lubricating greases," E. N. Klemgard, New York, Reinhold Publishing Corporation, 1937.

Other Sources of Motor Spirits

In the absence of crude petroleum, or to supplement it as a source of motor spirits, a number of materials and processes have been studied. In Germany, a country poor in petroleum resources, several methods were developed for manufacturing gasoline, naphthas and oils from coal. The complete liquefaction of coal by hydrogenation at rather low temperatures and high pressure, the method of Bergius, will yield about 40 gallons of motor spirits per ton of coal, besides 50 gallons of Diesel oil, 35 gallons of fuel oil, and 10,000 cubic feet of gas. In this process [52] the powdered coal is mixed with oil from a previous run to form a thick paste and heated to 400° C. (752° F.) in an atmosphere of hydrogen under the pressure of 150 atmospheres. In the I. G. process, the coal is hydrogenated in the presence of catalysts.

In England, the hydrogenation of bituminous coal, and of tar products from by-product coke ovens and coking retorts for city gas plants, is an established process; it is expected that there will be produced annually 30 million imperial gallons of motor fuel from coal, and 15 million gallons more from various tar products.[53] Since gasoline is 85 per cent carbon and 15 per cent hydrogen, while coal has only 5 parts hydrogen for each 85 parts, hydrogen to the extent of 10 parts per 90 parts of coal must be introduced. The process is a coal-in-oil phase which is pumped to the converter under pressure; the temperature is raised to 390° C. (734° F.) for half an hour, then to 450° C. (842° F.) for one hour. The product is separated into a heavy oil portion, which is hydrogenated further, the motor fuel fraction, and unreacted coal (5 per cent).

Synthetic Liquid Fuels and Chemicals

A number of circumstances and considerations, not the least among which is the increased peace-time consumption of liquid fuels, have invited the vigorous promotion in America of inventions and facilities for the manufacture of liquid fuels, mainly from "synthesis gas." The mixture of carbon monoxide and hydrogen which essentially constitutes the synthesis gas for liquid fuels, may be prepared from coal, by reaction with oxygen and steam simultaneously as was done in the German plants. It may also be prepared by a simpler method, namely by the controlled oxidation (or burning) of natural gas, the method favored in the United States, and the one which will be exemplified in the two full-scale plants now under construction, one in the Hugoton natural gas field at Garden City, Kansas, the other at Brownsville, Texas. Whatever the source, the process provides for the interaction of the carbon monoxide and hydrogen, with the aid of a catalyst. The manufacture of liquid fuels involves two steps: first, preparation of the synthesis gas, and second, the entirely distinct step of reacting the synthesis gas in the presence of a catalyst, at a preferred pressure and temperature. The

[52] U. S. Patent 1,592,772, to Friedrich Bergius.

[53] "Coal hydrogenation at Billingham," *Chem. Met. Eng.*, 42, 658 (1935), with 7 illustrations and 2 flow-sheets. See also "Oil," by F. Heron Rogers, Presidential Address, *Trans. Institution Chem. Eng.* (London), 18, 10 (1940).

following is a description of the operations planned at the Kansas plant.[54] The required oxygen will be the relatively cheap "tonnage oxygen," described in Chapter 19.

Preparation of the Synthesis Gas

Natural gas free of butane and heavier hydrocarbons but containing 22 per cent nitrogen is burned with oxygen at the rate of 109,000,000 cubic feet of gas a day. The oxygen is preheated to 600° F. (316° C.), the natural gas to 1200° F. (649° C.), and both enter the generator under a pressure of

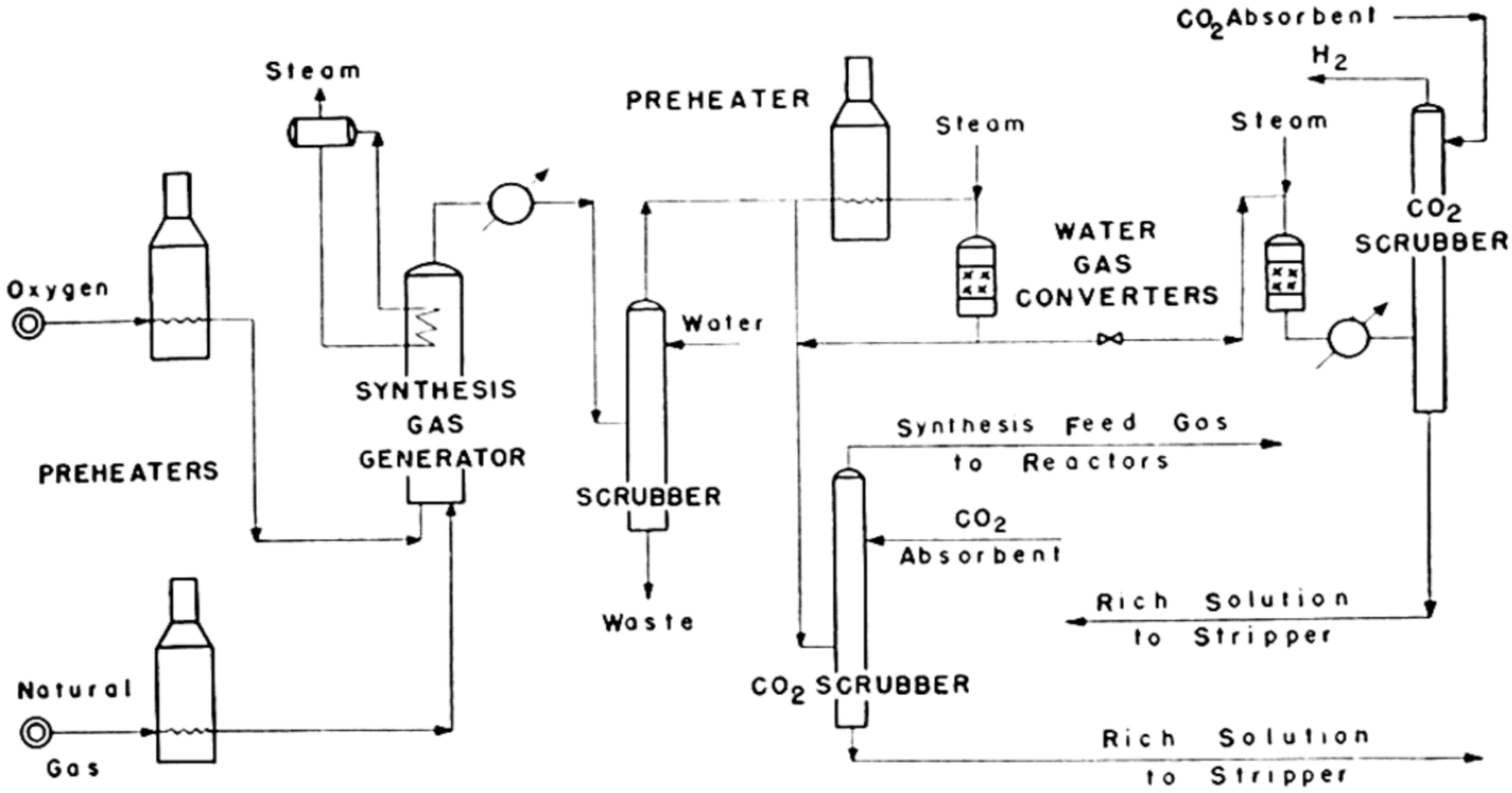


FIGURE 209.—Flow sheet for the generation of synthesis gas.
[*Chem. Eng. Progr.*, 44, 174 (1948).]

300 lbs/sq in. A definite ratio of oxygen to gas is maintained; there results a temperature in excess of 2400° F. (1316° C.). The outgoing hot gases are cooled under a waste heat boiler in which steam at 675 lbs/sq in. is generated, reaching a temperature of 600° F. (316° C.). They are cooled further by heat exchange and by cooling water; the reaction product water is condensed, and the gases enter a scrubber where any carbon particles present are removed (Figure 209).

In addition to natural gas and oxygen, a large amount of water is required for cooling purposes, steam generation and other plant uses; the amount is estimated at 250 million gallons a day. Most of the water will be re-used after passing through a large cooling tower, so that the make-up water will be held to about 10 million gallons a day.

[54] "Commercial application of hydrocarbon synthesis in the United States," James E. Latta and Scott W. Walker, *Chem. Eng. Progress*, 44, 173 (1948), supplemented by private communications from Dr. Latta, and the text of an address by Mr. A. L. Solliday, Vice President of Stanolind Oil and Gas Company, Tulsa, Okla. After this article had been prepared, there appeared a press notice dated August 22, 1948, in which Mr. E. F. Bullard, president of Stanolind, announced cancellation of the Garden City project, because of mounting costs of construction. The description of the process remains valid, nevertheless.

The principal reaction in the generator is:

$$\underset{\substack{\textit{Methane}\\ 1\text{ volume}}}{CH_4} + \underset{\substack{\textit{Oxygen}\\ \frac{1}{2}\text{ volume}}}{\tfrac{1}{2}O_2} \rightarrow \underset{\substack{\textit{Carbon monoxide}\\ 1\text{ volume}}}{CO} + \underset{\substack{\textit{Hydrogen}\\ 2\text{ volumes}}}{2H_2} \qquad (1)$$

In addition to reaction (1), a minor portion of the natural gas is oxidized more completely, *e.g.*:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O \qquad (2)$$

Reaction (2) is highly exothermic and must proceed to maintain the high reaction temperature in the gas generator. Therefore, the ratio of oxygen feed to natural gas feed volume is actually somewhat in excess of $\frac{1}{2}$ to 1 as

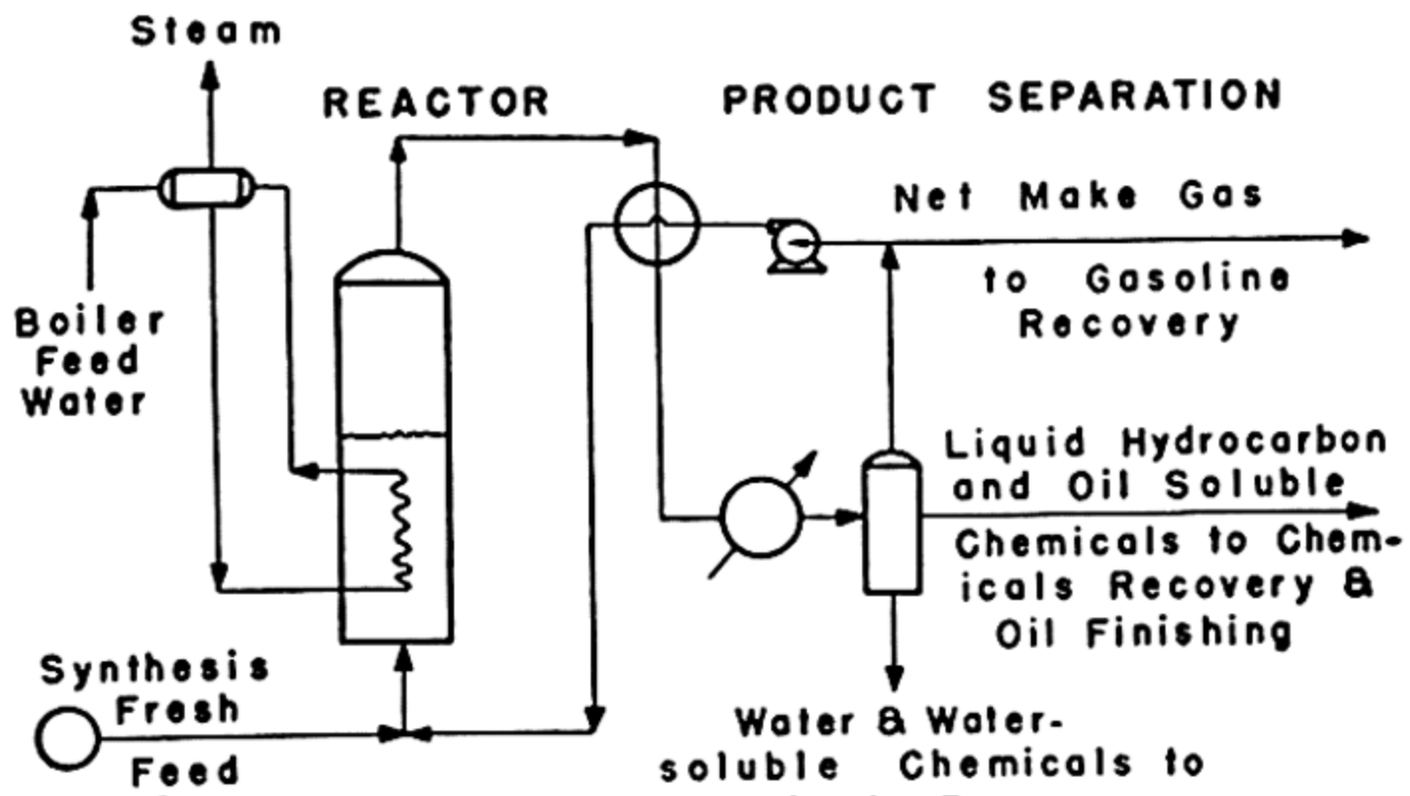


FIGURE 210.—Flow sheet for the synthesis reaction, producing liquid fuels and chemicals catalytically, from synthesis gas. [*Chem. Eng. Progr.*, 44, 175 (1948).]

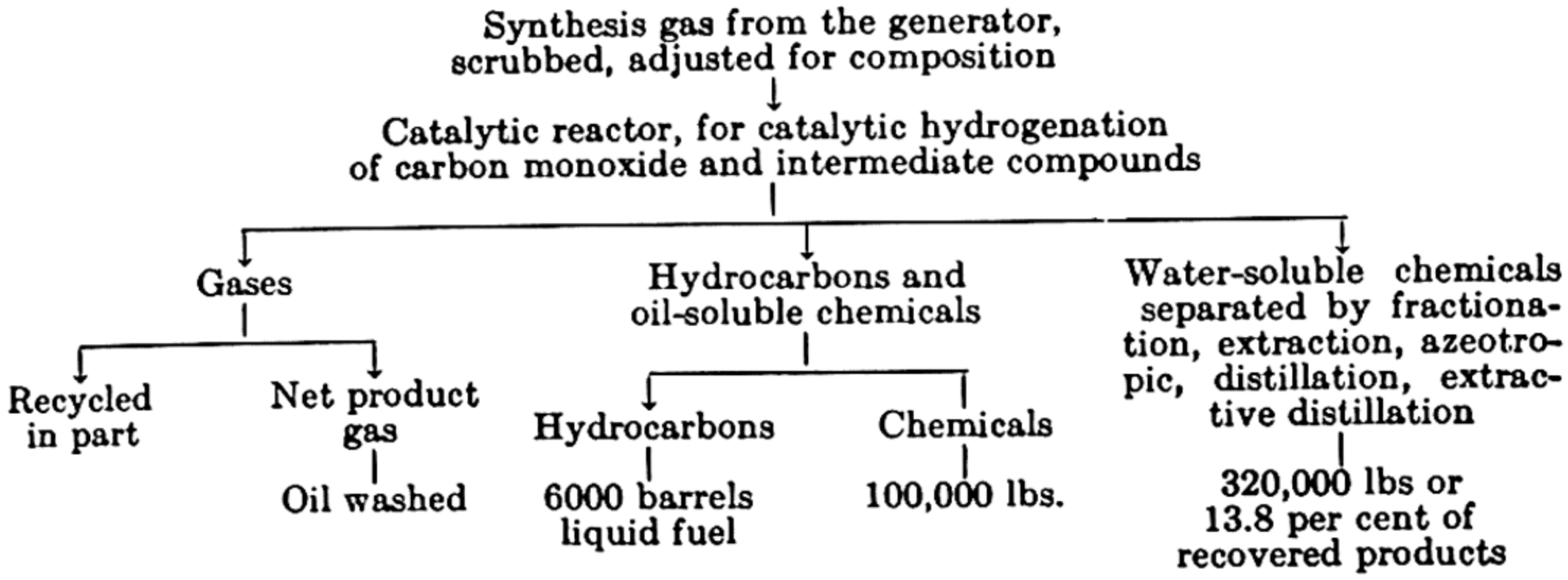
required by reaction (1). The effluent gases from the gas generator burning natural gas instead of pure methane contain the following: approximately 1.8 parts of hydrogen to 1 part of CO, the inert nitrogen in the feed gas, and minor amounts of CO_2 and H_2O from reaction (2).

A portion of the gas is preheated, mixed with steam, and passed over an impregnated iron oxide catalyst. The steam reacts with CO to produce more hydrogen (the water gas shift operation): $CO + H_2O \rightarrow H_2 + CO_2$. The enriched gas joins the main gas stream, which loses its CO_2 in an amine absorption tower. The synthesis gas is then ready for the reactor.

Catalytic Reaction of the Synthesis Gas

The reactor is a steel vessel with internal cooling provided by numerous small-diameter vertical pipes in which water circulates. The reactor contains the catalyst, an iron powder which the incoming gas stream entering at the base, keeps in suspension as a heavy cloud, constantly moving: the catalyst is fluidized. The exothermic reaction which takes place is a hydrogenation of the carbon monoxide, and of partly hydrogenated intermediate compounds, accompanied by polymerization. The products are hydrocarbons, oxygenated derivatives of hydrocarbons, carbon dioxide and water.

The vapors leaving the reactor are cooled and condensed and separated into gas, hydrocarbons, oil-soluble chemicals, and water-soluble chemicals (compare scheme below). The reactors operate at a pressure of 250 lbs/sq in., or at the most, 500 lbs.



The chemicals which may be recovered in all are 420,000 pounds per day, or 18 per cent of the total recovered products. The net product gas is scrubbed in oil, and recovered propylene and butylene are polymerized (solid phosphoric acid catalyst) with the production of about 1000 barrels of gasoline. The liquid hydrocarbons fraction is processed and separated into commercial grades of fuel, as for example into 5000 barrels of gasoline, 650 barrels of distillate fuel, and 280 barrels of fuel oil. The gasoline product contains olefins, which are especially high if the oxygenated oil-soluble compounds have been catalytically converted to hydrocarbons, so that its octane rating is approximately 80.

The nature of the product is influenced within certain limits by the composition of the feed gas, by temperature and pressure in the reactor, by the activity of the catalyst and the space velocity. Very high pressures favor a higher proportion of acids, alcohols and esters, while lower pressure, such as 7 atmospheres, favor a higher proportion of hydrocarbons.

The original method of producing liquid fuels and chemicals by the hydrogenation of carbon monoxide is the Fischer-Tropsch process, with coal as its primary material. Many processes employing a special catalyst and which differed otherwise have been proposed, and some of them were installed in Germany for full-scale operation. A valuable summary of all variations has appeared.[55]

It should be observed that the two types of products—hydrocarbons suitable for liquid fuels, and oxygenated compounds separable into useful chemicals—are produced unavoidably in the same reactor. The manufacturer who desires the liquid hydrocarbons finds that he has on his hands the chemicals fraction, which he must work up into marketable compounds,

[55] "The Synthine Process," B. H. Weil and John C. Lane, *Petroleum Refiner*, 25, 355-366, 423-434, 493-504, 587-598 (1946). See also "A summary of the latest developments and operating procedures of the Fischer-Tropsch process in Germany," Ernest Cotton, *National Petroleum News*, 38, R-425-34, June 5, 1946. For the Oxo process, see p. 545 and *Petr. Ref.*, 25, 503 (1946).

or delegate the assignment to some one else. On the other hand, the chemicals manufacturer who seeks alcohols, aldehydes, esters, and other chemicals, discovers that he must accept vast quantities of hydrocarbon compounds which are useful mainly as fuels. By changes in pressure, in temperature, in the composition of the synthesis gas or of the catalyst, and other variables the proportion of the two types of products may be varied to suit one's purpose, but only within certain limits; they continue to accompany each other. The proper procedure is to make a division of the product, and to work up the hydrocarbon portion in a petroleum refinery, and the oxygenated, water-soluble, chemicals portion in a chemical plant.

The catalyst in the German installations was cobalt with thoria as a promoter, a catalyst which favored a greater proportion of hydrocarbons at the expense of oxygenated compounds. The American iron powder catalyst containing an alkali oxide as a promoter produces a lower ratio of hydrocarbons with respect to the oxygenated compounds.

It is estimated that the cost of synthetic gasoline made by the liquid fuel process from natural gas, with the latter at the present price of 10 cents for 1000 cubic feet, would be about equal to the present petroleum gasoline price at the refinery of 12 cents a gallon. As to the supply of natural gas, it would appear that, allowing for the continued use of natural gas for other purposes as at present, there would be enough natural gas available for a number of years to produce about 350,000 barrels of synthetic gasoline a day, about 15 per cent of the total requirement. In default of natural gas, the far greater store of bituminous coal and other coal could be drawn upon and converted in plants which would, however, require a greater investment. At $2.50 a ton for coal, the cost of making gasoline is estimated at 16 to 17 cents a gallon. About 2.4 barrels of liquid fuel could be made from a ton of coal.

The installation expense required for the various kinds of processing plants is as follows: $2300 per barrel per day for petroleum oil; $5600 per barrel per day for natural gas made into liquid fuels and chemicals; $9000 per barrel per day for liquid fuels made from coal.[56]

Motor spirits from still other sources include industrial alcohol, which is suitable when mixed with petroleum distillates and a blending agent, to form a homogeneous liquid. Alcohol alone may be used, with a special carburetor, or alcohol-ether, a product made from molasses; the "alcoleter" of Cuba is such a motor spirit.

Oil shales are still another possible source.[57]

Ozokerite.

The name ozokerite originally designated an earth wax which was mined with pick and shovel. The dark raw material was purified to a white product which was not brittle (distinction from paraffin). The production was limited to certain deposits in Poland (Borislov) and in Russia (Baku). The

[56] E. V. Murphree, through Am. Petr. Inst.

[57] A flow sheet for a continuous shale retorting process will be found in "Process Handbook," *Petr. Ref.*, **27**, part 2, p. 76 (Sept., 1948).

products from the different districts did not have identical properties; they were, however, all amorphous solids consisting of large hydrocarbon molecules. The original ozokerite had good hardness, and blended well. Ozokerite as it was known 40 years ago is not at this time a commercially available product. The one wax which is now mined is Utah wax; after purification, Utah wax resembles the original ozokerite, except that it is brittle. In the course of the development of the petroleum industry it has been found possible to extract from settlings (tank bottoms) from a few selected crudes (southwest and middle west), by means of solvents, new waxes with properties similar to those of the original ozokerite, which have been named micro-crystalline waxes. Ceresin (today) is a blend of micro-crystalline wax and paraffin.

Petrochemicals

Petrochemicals are commercially pure chemical compounds of a single species, isolated or made by chemical reaction from any fraction of natural gas, wet natural gas or crude petroleum. No longer is petroleum merely a source of specialized fuels in which a mixture of chemical bodies, the chemical constitution of which matters little, is burned for their energy. The hydrocarbons themselves, concentrated and purified, are petrochemicals, as for example, ethylene, propane, butane, iso-butylene, normal hexane (a solvent), cyclohexane, toluene. Other somewhat more recent members are styrene and butadiene, discussed elsewhere in this book. One of the oldest members is ethyl alcohol, made from ethylene in competition with the product from fermentation.

Chemicals produced by one or more reactions, but based on a petroleum body, are petrochemicals.[58] Thus acetone, made by dehydrogenation of isopropyl alcohol, itself made by hydration of propylene produced in the refinery, is a petrochemical. One plant in Texas produces methanol, acetone, acetic acid, acetic anhydride, formaldehyde and acetaldehyde by the direct oxidation of propane and butanes. Pyrolysis, chlorination and nitration of the lighter hydrocarbons[59] lead to a constantly growing list of chemical substances, all petrochemicals. Nearly all the chemical bodies discussed in the next chapter would fall into this classification. The chemistry based on acetylene is an exception, but only insofar as the acetylene is the product of the electric furnace carbide process. If the acetylene is produced by pyrolysis of propane, for example, its derivatives again become petrochemicals.

The numerous chemicals produced incidental to the production of synthetic liquid fuels may all be properly regarded as petrochemicals.

An investigation of the isolation and identification of the hydrocarbons in petroleum by a large staff under the direction of Dr. Rossini has led to the separation of 72 hydrocarbons from a midcontinent crude oil.[60]

[58] "Basic oxygenated chemicals from C_1, C_2 and C_3 paraffins and olefins," John C. Walker and Howard L. Malakoff, *Petr. Ref.*, 25, 607 (1946).

[59] "Chemicals from lighter hydrocarbons," J. E. Bludworth, *Petr. Ref.*, 25, 216 (1946).

[60] "Hydrocarbons in petroleum," Frederick D. Rossini, *Chem. Eng. News*, 25, 230 (1947), with a list of the 72 hydrocarbons isolated. "Pure compounds from petroleum," Frederick D. Rossini, *Analytical Chemistry*, 20, 110 (1948).

An advantage possessed by the petrochemicals is that their source material is generally available in comparatively vast quantities, and is therefore generally less expensive than other materials.

A number of chemical substances are made by two methods, a standard and generally older method, and by a newer method employing a petroleum product as source, *i.e.*, phthalic anhydride, from a coal-tar product in the older method, from orthoxylene in the newer method. The reader should consult the index for proper reference to each of the substances mentioned in this section.

Other Patents

U. S. Pat. 2,169,809, alkylation of an isoparaffin with an olefin with sulfuric acid as agent; 2,432,482, alkylation process, by HF; 2,449,489, preparation of polymeric ethylene emulsions; 2,449,615, distillation of oil shale under fluidized conditions; 2,421,229, separation of isobutenes from a mixture of hydrocarbons; 2,420,883, process for the production of toluene; 2,360,787, the fluid catalyst process.

Problems

1. A storage tank for gasoline, with closed top equipped with a patent breathing valve, is 60-feet circular in diameter and 40 feet in height. It is designed for gasoline testing 55° A.P.I. at 60° F./60° F. How many gallons will it hold? How many gallons per inch of height? What is the weight in tons? A table of A.P.I. degrees and corresponding specific gravity will be found in the appendix.

2. In a "bulk plant," there is a storage tank 35 feet high, 25 feet in circular diameter, for the storage of kerosene of 40° A.P.I. at 60° F./60° F. How many gallons will it hold, and how many gallons for an inch of height?

3. In the same "bulk plant," another cylindrical tank is 25 feet in diameter and 30 feet in height. It holds a fuel oil testing 36° A.P.I. at 60° F./60° F. What is the capacity of the tank for this oil, and how many gallons per inch will it hold?

4. A pipe line delivers 5500 barrels of oil to a refinery in one day, at a regular rate over the 24 hours. The line is an 8-inch line. The oil is stored in 3 receiving tanks which are circular in cross-section, and 12 feet high. What size will the tanks have to be to hold one day's delivery? What is the velocity of the oil in the pipe, in feet per second? (Velocity × area = discharge.)

5. From the table of "Percentage yield of refined products" in the text, which represent weight relations, take the figures for each year and tabulate how much product by weight you would have produced every day from a daily crude input of 7800 gallons. For the gasoline, kerosene, and fuel oil lines, compute the volume, taking the A.P.I. densities as given in prcblems 1, 2, and 3.

Reading References

"Symposium on petroleum discovery methods," *J. Am. Assoc. Petroleum Geologists*, April, 1942.

"When oil wells run dry," Walter M. Fuchs, Dover, N. H., Industrial Research Service, 1946.

"Done in oil," *Petroleum Encyclopedia*, David D. Leven, New York, The Ranger Press, 1942.

"Acid solvents for oil wells: physicochemical properties adapted to various production conditions," L. C. Chamberlain, Jr., and R. F. Boyer, *Ind. Eng. Chem.*, 39, 400 (1939).

"The chemical control of gaseous detonation with particular reference to the internal-combustion engine," T. E. Midgley, Jr., and T. A. Boyd, *Ind. Eng. Chem.*, 14, 894 (1922).

"The refining process with liquid sulfur dioxide," Dr. L. Edeleanu, *J. Inst. Petroleum Tech. (London)*, 18, 900 (1932).

"The Edeleanu process for refining petroleum," R. L. Brandt, *Ind. Eng. Chem.*, 22, 218 (1930).

"The use of liquid propane in dewaxing, deasphalting and refining heavy oils," Robert E. Wilson, P. C. Keith, Jr., and R. E. Haylett, *Trans. Amer. Inst. Chem. Eng.*, 32, 364 (1936), or *Ind. Eng. Chem.*, 28, 1065 (1936).

"Solvent extraction processes," R. E. Hersh, *Petroleum News*, 30 (Nov. 4, 1936).

"Products of polymerization, benzene, toluene and xylene are produced by thermal polymerization in addition to motor fuel," C. M. Ridgeway, C. R. Wagner and H. R. Swanson, *Petroleum News*, 47 (Nov. 4, 1936).

"Hydrogenation of American coals," W. L. Beuschlein and C. C. Wright, *Ind. Eng. Chem.*, 24, 1010 (1932).

"Hydrogenation tests on Canadian coal," T. E. Warren and R. E. Gilmore, *Ind. Eng. Chem.*, 29, 353 (1937).

"Hydrogenation of coal," W. Idris Jones, *J. Soc. Chem. Ind.*, 53, 321 (1934).

"Coal hydrogenation, a comparison of coal and oil," M. Pier, *Ind. Ing. Chem.*, 29, 140 (1937).

"Critical analysis of sweetening processes and mercaptan removal," John Happel, S. P. Cauley and H. S. Kelly, *Petr. Ref.*, 21, 406 (1942).

"Recent developments in TCC processing," T. P. Simpson, L. P. Evans, C. V. Hornberg and J. W. Payne, *Petr. Ref.*, 22, 353 (1943).

"The design and operating features of Houdry fixed bed catalytic cracking units," R. H. Newton and H. G. Shimp, *Trans. Am. Inst. Chem. Eng.*, 41, 197 (1945).

"The TCC catalytic cracking process for motor gasoline production," R. H. Newton, G. S. Dunham and T. P. Simpson, *Trans. Am. Inst. Chem. Eng.*, 41, 215 (1945).

"The Thermofor catalytic cracking process," T. P. Simpson, L. P. Evans, C. V. Hornberg and J. W. Payne, *Petr. Ref.*, 21, 401 (1942).

"Simplicity and flexibility of Thermofor catalytic cracking," H. D. Noll, K. G. Holdon, and E. V. Bergstrom, *Petr. Ref.*, 25, 237 (1946).

"Catalytic cracking of petroleum oils," description of a fluid catalyst plant at Anglo-Iranian Oil Company Research station at Sunbury-on-Thames, D. A. Howes, *The Industrial Chemist (London)*, 23, 217 (1947).

"Postwar petroleum refinery operations," E. R. Smoley and V. O. Bowles, *Petroleum Engineer* (May, 1945).

"Conversion of petroleum, production of motor fuels by thermal and catalytic processes," A. N. Sachanen, New York, Reinhold Publishing Corporation, 2nd ed., 1948.

"A fluid-catalytic cracking unit for the smaller refiner," Davis Read, *Petr. Ref.*, 25, 233 (1946).

"Fluid catalyst cracking for premium fuels," E. V. Murphree, H. G. M. Fischer, E. J. Gohr, W. J. Sweeney, and C. L. Brown, *Petr. Ref.*, 22, 357 (1943).

"Extractive and azeotropic distillation. I. Theoretical aspects," Manson Benedict and Louis C. Rubin, *Trans. Am. Inst. Chem. Eng.*, 41, 353 (1945), and "II. Separation of toluene from paraffins by azeotropic distillation with methanol," Manson Benedict, C. A. Johnson, Ernest Solomon and Louis C. Rubin, *Ibid.*, 41, 371 (1945).

"The production of toluene from petroleum," D. A. Howes, *Ind. Chemist*, 32, 403 (1946).

"Reactor design for manufacture of toluene by catalytic reforming," A. A. Burton, E. B. Chiswell, W. H. Claussen, C. S. Huey and J. F. Senger, *Chem. Eng. Progress*, 44, 195 (1948).

"Potential use of hydrogen fluoride in organic chemical processes," J. H. Simons, *Ind. Eng. Chem.*, 32, 178-183 (1940).

"The development of the hydrogen fluoride alkylation process," G. G. Gerhold, J. O. Iverson, H. J. Nebeck, R. J. Newman, *Trans. Am. Inst. Chem. Eng.*, 39, 793 (1943).

"Experiences in the commercial application of the hydrogen fluoride alkylation process," Emory M. Skinner, *Trans. Am. Inst. Chem. Eng.*, 41, 647-670 (1945).

"Symposium, 46 papers on fluorine," beginning on p. 236, *Ind. Eng. Chem.*, 39 (1947).

"Corrosion in hydrofluoric acid alkylation," M. E. Holmberg and F. A. Prange, *Ind. Eng. Chem.*, 37, 1030 (1945).

"Rôle of water in conquering fire in refining plants," Dawson Powell, *Petr. Ref.*, 25, 513 (1946).

"Furfural extractive distillation, for separation and purification of C_4 hydrocarbons," C. K. Buell and R. G. Boatright, *Ind. Eng. Chem.*, 39, 695 (1947).

"Separate processing for rich and lean gas," *Petr. Ref.*, 25, 220 (1946).

"High pressure absorption" (of natural gasoline values), Henry F. Wade, *Petr. Ref.*, 25, 206 (1946).

"Cycling plants stabilize crude oil," G. M. Liljenstein, *Petr. Ref.*, 27, 505 (1948).

"Modern process methods to improve L.P.G. recovery," G. W. McCullough, K. H. Hachmuth, and A. J. Miller, *Petr. Ref.*, 27, 166 (1948).

"Diesel fuel characteristics influencing engine output," A. J. Blackwood and G. H. Cloud, *J. Inst. Petr.*, 25, No. 192 (1939).

"Diesel fuels; more complex refining seen . . .," J. R. MacGregor, G. R. MacPherson and P. L. Pinotti, *Petr. Ref.*, 27, 365 (1948).

"Diesel fuels from catalytic cracking operations," T. L. Apjohn and F. L. Nelson, *Petr. Ref.*, 27, 346 (1948).

"Hydroforming for production of high-octane motor fuel," L. R. Hill, G. A. Vincent and E. F. Everett, *Trans. Am. Inst. Chem. Eng.*, 42, 611 (1946).

"The isomate process," J. E. Swearingen, R. D. Geckler and C. W. Hysewander, *Trans. Am. Inst. Chem. Eng.*, 42, 573 (1946).

"Isomerization of light hydrocarbons," by Stephen F. Perry, *Trans. Am. Inst. Chem. Eng.*, 42, 639 (1946).

"Butane isomerization," J. A. Chenicek, J. O. Iverson, R. E. Sutherland and P. C. Weinert, *Chem. Eng. Progress*, 43, 210 (1947).

"Naphtha polyforming," W. C. Offutt, P. Ostergaard, M. C. Fogle and H. Beuther, *Petr. Ref.*, 25, 554 (1946), and the two adjoining articles.

"British Aviation Fuel Manufacture in the Middle East. Part III. New Plants by the technical staff of the Anglo-Iranian Oil Co. Ltd.," *Ind. Chem.*, 22, 586 (1946).

"Synthesis and properties of hydrocarbons of high molecular weights," R. W. Schiessle, J. N. Crosby, D. G. Clarke, C. W. Roland, W. S. Sloatman, C. H. Herr, *Petr. Ref.*, 21, 383 (1942).

"Vacuum distillation of petroleum residues," W. W. Kraft, *Ind. Eng. Chem.*, 40, 807 (1948).

"Asphalt and allied substances," H. Abraham, New York, D. Van Nostrand Co., 4th edition, 1938.

"The chemistry and technology of waxes," Albin H. Warth, New York, Reinhold Publishing Corporation, 1947.

"Review of development of processes for synthesis of liquid fuels by hydrogenation of carbon monoxide," H. H. Storch, *Chem. Eng. Progress*, 44, 469-480 (1948).

"Petrochemicals," Gustav Egloff, *Oil & Gas J.*, 46, No. 17, pp. 88-97 (1947).

"Acetylene and Carbon Monoxide Chemistry," J. W. Copenhaver and M. Bigelow (a complete survey and evaluation of the Reppe chemistry), New York, Reinhold Publishing Corp., 1949.

"Petrochemicals at Corpus Christi," *Chem. Industries*, 62, 738 (1948).

There was a time not so long ago when the chemist sought exclusively for natural products so that he might extract or distill from them the complicated molecules containing carbon, hydrogen, and oxygen or nitrogen. The distillates or extracts were chemicals originating in nature's laboratory, in living systems, vegetable or animal; they were therefore called "organic." It was with reverence that the chemist isolated such chemicals. Today, he is bolder. Natural sources are still sought and utilized, but in addition, the chemist or engineer uses coal and limestone, for example, and produces from them the delicate and volatile acetate esters. This makes true the slogan: From rocks to ethereal solvents. But it is well to note at once that even in these bold syntheses, all the worker does is to provide the circumstances and conditions so that the laws of nature may function to his advantage. At no time does he make nature do his will; the achievement is rather in the discoveries of a few of those laws; the attitude of humility before the laws of nature is still in order.

Chapter 25

Synthetic and Semi-Synthetic Organic Chemicals

In the course of the last fifty years, many synthetic organic chemicals have been brought to the commercial state and have entered the economic life of the world. During and after World War I much progress was made; witness the synthetic aldehyde and acetic acid derived from acetylene. By catalytic hydration, acetaldehyde is formed, and this in turn by catalytic oxidation, yields acetic acid—a synthetic acetic acid—able to replace in all its uses the older acetic acid from wood distillation. Of more recent date, are the chemicals built on ethylene (CH_2:CH_2) as starting material; they include ethylene glycol and the glycol ethers.

World War II accelerated the work of synthesis. Such an organic synthetic chemical as ethylbenzene for the production of styrene was and still is manufactured by the hundreds of tons, and all the other derivatives of ethylene are made in large quantities. The chemistry of acetylene has been further extended by German workers, in part under the stress of war necessity. A third important starting material is carbon monoxide, which reacts with hydrogen in the presence of a catalyst to form hydrocarbons and oxygenated carbon compounds, all in the truest sense "synthetic organic chemicals" even though some of them are treated in the previous chapter under the head of petroleum and its products.

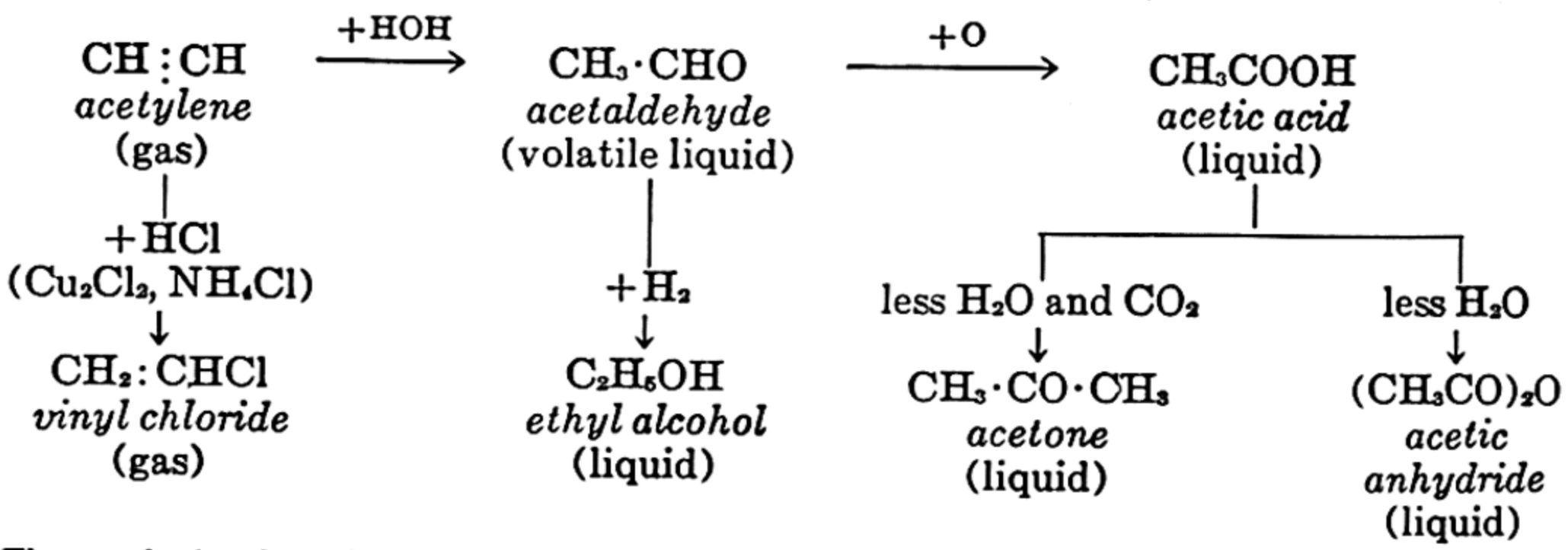
The three series derived from acetylene (ethyne), ethylene (ethene) and carbon monoxide, respectively, represent the synthetic chemicals. What might be called semi-synthetics are the chemicals resulting from partial or controlled oxidation of natural products, chiefly with the aid of a contact substance: for example, phthalic anhydride from naphthalene, maleic anhydride from benzene. Another semi-synthetic group is hydrogenation products, *i.e.*, the hydrogenated vegetable oils, which become "vegetable fats," by the addition of hydrogen to the molecule.

A number of synthetic and semi-synthetic substances, of value in the perfume industry, are described in Chapter 30. Synthetic amyl alcohol from pentane is included in Chapter 20.

Chemicals Based on Acetylene (Ethyne) as Starting Material

Acetylene in its role of industrial gas has been described in Chapter 19, where its generation from calcium carbide on an industrial scale and its manufacture from other sources are discussed. Acetylene, the chemical,

Table 94.—*Relation of certain acetylene chemicals,* First Part.*



* The synthesis of acetic acid from acetylene was worked out for large-scale operation by a group of scientists at Shawinigan Falls, Quebec, Canada, during the war emergency of 1914-18 and had as its chief aim the manufacture of acetone, required in the production of munitions. A survey of the early achievements will be found in "Synthetic acetic acid and acetone," J. T. Rooney, *Chem. Met. Eng.*, 22, 847 (1920).

undergoes a number of reactions, among them that of hydration, with the production of acetaldehyde.

Acetaldehyde. For the manufacture of acetaldehyde (CH_3CHO), a low-boiling liquid, soluble in water, acetylene gas from the holder or directly from a manifold connected to the generators, is fed into a solution of mercuric sulfate with some dilute sulfuric acid, contained in the reaction vessel made of Duriron, with a conical bottom, and surmounted by a short plate tower. Once the reaction has started, the liquid reaction mixture contains acetaldehyde, acetylene, the catalyst mercuric sulfate (in this example), and finely divided mercury accompanied by insoluble mercury-organic bodies. The gas enters at the bottom at a steady rate and keeps the thin sludge well stirred; its volume is greatly in excess of the amount which is to react. At a rate corresponding to the reaction, air-free, luke-warm water is fed in. The function of the unreacted acetylene gas is to sweep out the product. Periodically a part of the sludge is removed, and a charge of fresh mercuric sulfate in air-free water is supplied. The reaction

$$C_2H_2 + H_2O \rightarrow CH_3CHO$$

is exothermic, so that heat must be removed by cold water circulating in a coil placed in the reaction vessel. The temperature is maintained at 68° C. (154° F.) at which acetaldehyde passes out freely, carrying with it a certain amount of water vapor. In the plate tower, cooling causes condensation of a water solution of aldehyde, which becomes stronger the higher the plate. Acetaldehyde, water, acetylene, and several other minor reaction

products in smaller quantities pass out at the top; the vapors pass upward in a circular box with cooling coils. A water solution of acetaldehyde containing about 20 per cent water is collected and stored in aluminum tanks; the acetylene gas passes out and after purification joins the makeup gas on its way to the reaction vessel. Pure acetaldehyde boils at 20° C. (68° F.) at atmospheric pressure.

There were produced in the United States in 1946 351,916,000 pounds of acetaldehyde of which 18,882,000 pounds reached the market, at 8 cents a pound; in 1947, the production was 424,645,000 pounds at 9 cents a pound (Tariff Commission).

Acetic Acid. Several chemicals are formed from acetaldehyde directly: acetic acid, ethyl acetate, butyl acetate, acetic anhydride, while acetic acid and acetylene may be made to yield acetic anhydride, all by catalytic reactions.

For acetic acid, a batch process [1] is as follows. A thousand gallons of acetaldehyde from the acetylene hydration, rectified so that its water content is very low, are pumped into an aluminum-lined reaction vessel provided with coils for water or steam. To this 0.5 per cent manganese sulfate or acetate is added, and air (300 cu. ft. per minute) blown in against the pressure at which the reaction vessel is operated, about 3 atmospheres. The temperature is raised to 25° C. (77° F.), which is below the boiling point of acetaldehyde at the pressure used. As the reaction gets under way, the temperature rises to 65° C. (149° F.) and the pressure to 75 pounds:

$$2CH_3\cdot CHO + O_2 \rightarrow 2CH_3\cdot COOH.$$

Nitrogen is allowed to escape through a brine-cooled separator, which retains the entrained aldehyde and acid. The reaction is complete in 8 to 12 hours, when the charge is distilled, then redistilled with the aid of a plate column, operated continuously and yielding 99 per cent acetic acid.

The function of the manganese catalyst is not to catalyze the oxidation of the aldehyde, but rather to decompose an intermediate product, per-acetic acid, which is explosive; as it decomposes, the desired acetic acid forms. The higher manganese oxide formed attacks fresh acetaldehyde:

$$CH_3\cdot CHO + O_2 \rightarrow \underset{\textit{per-acetic acid}}{CH_3\cdot CO\cdot O\cdot OH}$$

$$CH_3\cdot CO\cdot O\cdot OH + MnO_2 \rightarrow CH_3\cdot COOH + \underset{\textit{brown color}}{MnO_3 \text{ or intermediate oxides}}$$

$$MnO_3 \text{ or intermediate oxides} + CH_3\cdot CHO \rightarrow CH_3\cdot COOH + MnO_2$$

Ethyl Acetate from Acetaldehyde. In the presence of small amounts of aluminum ethylate, $Al(C_2H_5O)_3$, and aluminum chloride, $AlCl_3$, acetaldehyde is transformed to ethyl acetate with a recovery of over 90 per cent:

$$2CH_3CHO \rightarrow CH_3\cdot COOC_2H_5.$$

At the present time, ethyl acetate is made almost exclusively from fermentation alcohol and acetic acid from various sources, but the process just given may gain industrial importance in the future.

[1] English Patent 132,558 (1918), class II, 3, p. 91 abridgments; 132,557 (1918), class II, 3, p. 90 abridgments.

Acetic Anhydride from Ethylidene Diacetate. If instead of passing acetylene into a water suspension of mercuric sulfate, as is done in the fundamental process in this series, it is passed into a suspension of mercuric sulfate in concentrated or glacial acetic acid, using the same kind of reaction vessel, there is formed ethylidene diacetate. (The ethylidene radical is $CH_3CH:$).

$$C_2H_2+2CH_3\cdot COOH \rightarrow CH_3CH(O\cdot CO\cdot CH_3)_2.$$

On distilling this product in the presence of small quantities of anhydrous salts or agents, such as zinc chloride or sodium pyrophosphate, $Na_4P_2O_7$, the diacetate decomposes into acetaldehyde and acetic anhydride:

$$CH_3\cdot CH(O\cdot CO\cdot CH_3)_2 \rightarrow CH_3\cdot CHO+O(CO\cdot CH_3)_2.$$

The distillation may be performed at reduced pressure (100 mm.) and 80° C. (176° F.), or at atmospheric pressure and 130° C. (266° F.). The acetaldehyde may be used over again in the acetic acid synthesis.

It has been found advantageous to introduce the decomposing agent, such as phosphoric acid, in small lots [2] at suitable intervals into the boiling ethylidene acetate, in order to avoid forming acetic acid or tars. The conversion is 87.4 per cent. In the subsequent distillation, unchanged ethylidene acetate is left behind; the distillate is fractionated and furnishes 80 to 90 per cent acetic anhydride, the customary commercial strength.

Acetic Anhydride from Acetic Acid. Acetic anhydride may be made directly from glacial acetic acid by passing it in vapor form over granules of catalyst [3] kept at 600° to 620° C. (1112° to 1148° F.). The catalyst is made by mixing 200 grams of sodium ammonium phosphate, $NaNH_4HPO_4$ with 1000 grams of boron phosphate; the yield is 48 to 50 per cent.

A more recent method consists of reacting ketene ($CH_2:C:O$), a gas produced by the pyrolysis of acetone

$$CH_3\cdot CO\cdot CH_3 \rightarrow CH_2:C:O+CH_4,$$

with acetic acid

$$CH_3COOH+CH_2:C:O \rightarrow CH_3CO\cdot O\cdot OCCH_3.$$

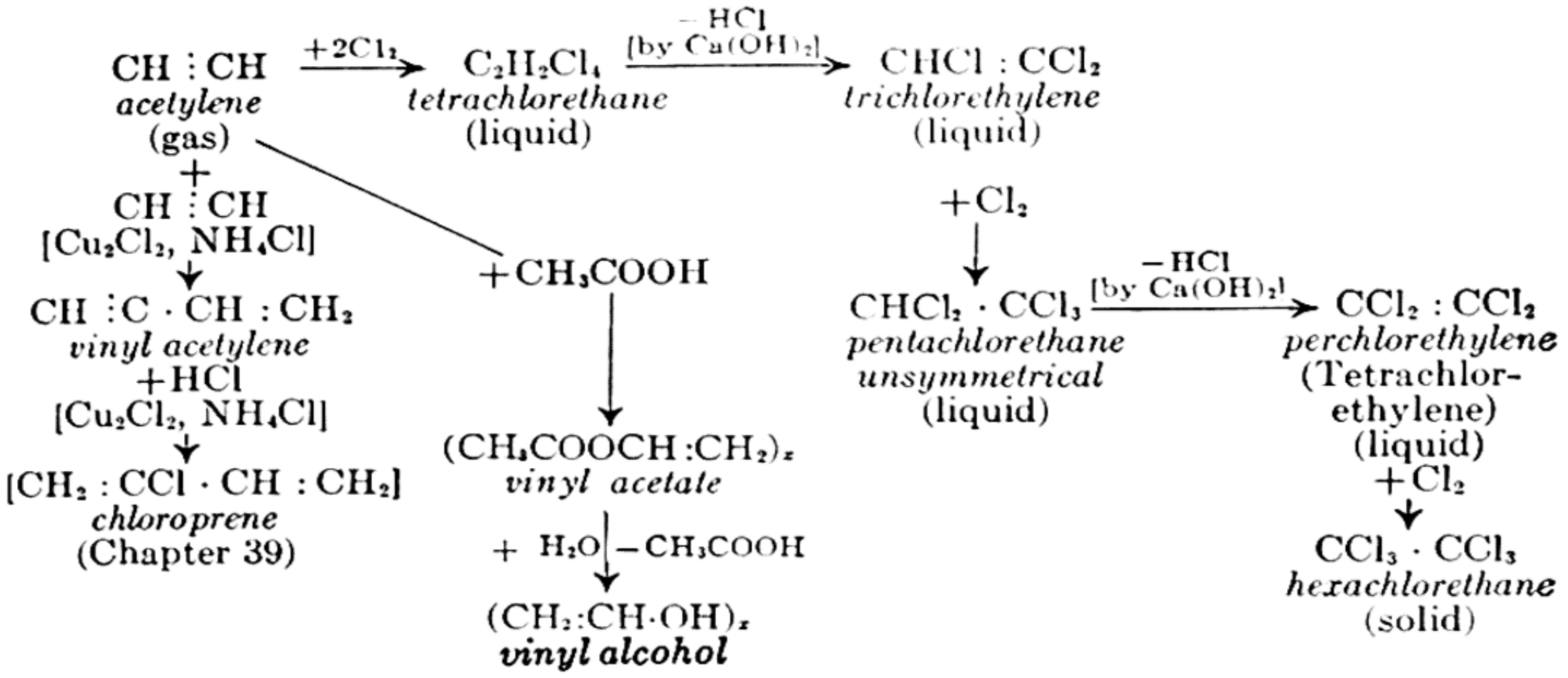
(Compare Chapter 16.)

The production of synthetic acetic acid in the United States in 1946 was 285,452,000 pounds; the portion sold brought 8 cents per pound. In 1947, the production had risen to 362,463,000 pounds, valued at 9 cents a pound (Tariff Commission).

Chlorinated Hydrocarbons. By the chlorination of acetylene to tetrachloroethane, followed by the removal of hydrogen chloride, trichloroethylene is formed. It is a liquid which has become an important solvent, and is now made at the rate of many tons a day. By chlorination, with subsequent hydrogen chloride removal, and again chlorination, three more chlorinated hydrocarbons are formed, as shown in Table 95.[4]

[2] U. S. Pat. 1,578,454.
[3] U. S. Pat. 1,870,357.
[4] *Compare* "An R. & H. Technical Bulletin," "Chlorinated Hydrocarbons," (1935), The R. & H. Chemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

TABLE 95.—*Relation of certain acetylene chemicals, Second Part.*



Another important branch of the acetylene chemicals family is the vinyl compounds. A stream of acetylene in acetic acid gives *vinyl acetate* which may then be polymerized to various degrees, after which it is hydrolized to give polyvinyl alcohol,[5] a water-soluble solid. Polyvinyl alcohol is used to diminish the "drag out," that is, the volume of liquid carried out by the metal objects on being removed from the bath. There is a growing list of other uses. Acetylene to form chloroprene, 2-chlor-1, 3-butadiene, is presented in Chapter 39.

Acetylene heated to about 230° C. in contact with copper condenses to a chemically inert, light, cork-like solid called cuprene.[6]

Degreasing Metal Surfaces. An important use of certain of the newer solvents is in the degreasing of metal surfaces, preparatory to coating them with another metal, by electrolysis, by dipping, or in some other way. Trichloroethylene particularly is favored, and not only its uses, but several methods for performing the degreasing, with the apparatus, have been the subject of patents.[7] In one system, the cold metal parts are suspended in the vapor of the solvent, which recondenses on the walls of the same vessel, extended to form a short reflux column; only the pure solvent, with maximum solvent power, reaches the objects. The solvent is kept warm by a steam coil. The vapors do not escape, thanks to their great weight relative to air. In order to prevent corrosion, a "stabilizer" is added; this may be 0.001 per cent triethylamine,[8] 0.05 per cent to 0.1 per cent amylene,[9] or, less satisfactory, gasoline.[10]

[5] U. S. Patent 1,942,531.
[6] "The Chemistry of Acetylene," J. A. Nieuwland and Richard R. Vogt, New York Reinhold Publishing Corp., 1945.
[7] U. S. Patents 1,906,968; 1,961,867; 1,875,937; 1,938,841; 1,869,845; and 1,869,826.
[8] U. S. Patent 1,911,826.
[9] U. S. Patent 1,904,450.
[10] U. S. Patent 1,816,895.

Reactions of Acetylene under Pressure and at Ordinary Pressure; the Reppe Chemistry

In the several processes for acetylene reaction just described, the gas is used under moderate pressure, generally under one atmosphere (that is, under 15 lbs. gauge). Work at higher pressures was not pressed, at least in the United States, partly because of the safety hazard, and partly because there was no urgent need for the possible products. It was different in Germany where ethylene, for example, is not plentiful, and where the variety of raw materials available to American industry is lacking. Out of this need have come (1) a hydrogenation process to produce ethylene, on which in turn all the standard ethylene chemistry could be based; (2) a method for making the sorely needed butadiene from acetylene; (3) a number of novel reactions in which acetylene is added to the molecule, forming vinyl esters, vinyl ethers, vinyl thioethers, vinyl ammonium bases, vinylamides and others. This work with acetylene under pressure and at elevated temperature broke essentially new ground.

Therefore, for the successful carrying out of this research, it was necessary to dismiss all the over-worked traditions concerning the danger of acetylene under pressure as well as a considerable portion of the published information, and to study the decomposition of acetylene from the ground up, observing the effect of various reaction conditions such as pressure temperature, mixing of inert gases, and mixing of the vapors of various reaction components, etc., and to carefully determine the explosion limits. . . . . this work has proven very fruitful, and above all has placed us in a position to operate without danger on a technical scale." [11]

Ethylene is made by passing acetylene, mixed with twice the theoretical amount of hydrogen, and with steam, over palladium on a silica gel carrier at a temperature of 270° C. (518° F.) under ordinary pressure. The ethylene obtained by this partial hydrogenation became the starting point (in the German technology) for all of the ethylene chemicals, including styrene.

The manufacture of butadiene directly from acetylene is undoubtedly the most striking achievement of the new acetylene technique. The synthesis in its first step involves acetylene, formaldehyde and water.[12] A water solution of formaldehyde (30 per cent CHOH) and a large excess of acetylene are passed through the reactors under a pressure of 5 atm., at temperatures between 80 and 120° C. (176 to 248° F.), to form butynediol. The reactors are towers 60 feet in height and 5 feet (1½ meters) in diameter, containing the catalyst (copper acetylide) on silica granules. The towers are the largest pressure towers ever built for catalytic processes. Two reactors are

[11] Dr. Julius Walter Reppe, in an address (July 26, 1940) describing the work at Ludwigshaven, quoted through PB-13366, Office of the Publication Board, now Office of Technical Services, Dept. of Commerce, Washington, D. C. The numerous "diagrams" (charts) to which Dr. Reppe refers, are missing. See also Ref. 1.

In the interest of safety, acetylene is diluted with inert gases, which retard the propagation of an otherwise explosive reaction. In certain reactions, such as in some of the ethynylations, the hot concentrated gas must be used; the safety measure applied there is to reduce all free spaces to a minimum, again in order to interfere with the propagation of an otherwise explosive decomposition.

[12] Intelligence Division Report 4149, p. 32.

used in series, and the conversion is nearly complete in one pass, with an excellent yield. The high heat of formation is dissipated by evaporation of water and by the cyclic pumping of the acetylene excess under pressure. This first step is an *ethynylation*, that is, a process which results in the introduction of the ethynyl group, HC:C—, into the molecule.

$$\underset{\textit{acetylene}}{HC{:}CH} + \underset{\textit{formaldehyde}}{2HCHO} \rightarrow \underset{\substack{\textit{3-butynediol-1,4}\\(\text{a solid, m.p. } 64^\circ \text{ C.})}}{HO{\cdot}CH_2{\cdot}C{:}C{\cdot}CH_2{\cdot}OH}$$

The butynediol is purified by distillation, and perhydrogenated (copper nickel on silica catalyst, 300 atm., 100° C.) giving 1,4-butynediol, which is then dehydrated to tetrahydrofuran, after addition of 0.1 per cent acid to the water solution, and treatment at temperatures of 250-300° C. (482-572° F.) under a pressure of about 100 atm.

$$\underset{\textit{3-butynediol-1,4}}{HO{\cdot}CH_2{\cdot}C{:}C{\cdot}CH_2{\cdot}OH} + 2H_2 \rightarrow \underset{\substack{\textit{1,4-butanediol}\\(\text{m.p. } 16^\circ \text{ C.})}}{HO{\cdot}CH_2CH_2CH_2CH_2{\cdot}OH} \rightarrow \underset{\substack{\textit{tetrahydrofuran}\\(\text{a liquid})}}{\begin{array}{l}CH_2CH_2\\ \quad O \\ CH_2CH_2\end{array}} + H_2O$$

The tetrahydrofuran in turn is dehydrated to butadiene.

$$\begin{array}{l}CH_2CH_2\\ \quad O \\ CH_2CH_2\end{array} \xrightarrow[\text{phosphate catalyst}]{260\text{-}280^\circ \text{ C.}} \underset{\textit{butadiene-1,4}}{CH_2{:}CH{\cdot}CH{:}CH_2}$$

The butynediol is accompanied by about 2 per cent propargyl alcohol ($HOCH_2{\cdot}C{:}CH$) a liquid, which can undergo 10 or more reactions leading to useful products. Butanediol is an intermediate for the preparation of polyamide intermediate products. Tetrahydrofuran is not only the parent substance to butadiene, but is itself an intermediate of great value; from it may be made, for example, adipic acid, by two different paths, and hexamethylenediamine, both raw materials for nylon salt. (Compare Chapter 22.)

Another older process successfully introduced for the synthesis of butadiene rests, at least indirectly, on acetylene, since its starting point is synthetic acetaldehyde. The four steps are: acetldehyde, aldol, the reduction of the latter to butanediol, and 1,3-butadiene.

The *vinylation* of alcohols with potassium alcoholate as catalyst runs smoothly; only for the lower-boiling members is pressure necessary. For producing vinylmethyl ether [b.p. 9° C. (48° F.)] by a continuous operation a pressure of about 15 atm. is employed; for vinylethyl ether, 10 atm., and for vinylisobutyl ether, 3 atm. In the interest of safety, the acetylene is diluted with nitrogen.

$$\underset{\substack{\textit{Potassium}\\\textit{alcoholate}}}{C_2H_5OK} + \underset{\textit{acetylene}}{CH{:}CH} \rightarrow \underset{\textit{addition body}}{C_2H_5O\text{-}CH{:}CHK} \qquad (1)$$

$$C_2H_5O\text{-}CH{:}CHK + C_2H_5OH \rightarrow \underset{\textit{vinylethyl ether}}{C_2H_5O\text{-}CH{:}CH_2} + \underset{\substack{\textit{regenerated alcoholate}\\(\text{acts further})}}{C_2H_5OK} \qquad (2)$$

The vinyl esters of higher fatty acids are obtained by the action of acetylene on the acids containing 1 to 3 per cent zinc oxide, which forms the zinc salt. The acetylene enters between the metal and the oxygen to form an addition compound, which then reacts with more acid to give the final vinyl ester and reform the zinc salt.

Reactions of acetaldehyde with acetylene, on one side of the molecule, and on both sides, are among the many new chemical combinations which in turn lead to many others.[13]

$$(R\cdot COO)_2Zn + 2C_2H_2 \xleftarrow[\text{with low mol. wt. fatty acids}]{180^\circ\text{ C.}} (R\cdot COOCH{:}CH)_2Zn$$

$$(R\cdot COOCH{:}CH)_2Zn + 2R\cdot COOH \rightarrow 2R\cdot COOCH{:}CH_2 + (R\cdot COO)_2Zn$$

vinyl ester

$$CH_3\cdot \underset{\underset{O}{\cdot\cdot}}{C}\cdot H + C_2H_2 \xrightarrow[\substack{\text{Cu acetylide}\\ 100^\circ\text{ C.}}]{3\text{ atm.}} CH_3\cdot \underset{\underset{H}{O}}{C}\cdot C{:}\,CH$$

an alkyneol

Other reactions also produce chemicals which are themselves the starting material for a long line of derivatives, all of technical importance. The first one which follows is an example of *carboxylation.*

$$C_2H_2 + CO + H_2O \xrightarrow[HCl]{Ni(CO)_4} CH_2{:}CH\cdot COOH$$

acrylic acid (m.p. 12°C.)

$$C_2H_2 + HCN \xrightarrow[Ba(CN)_2]{\text{heat}} CH_2{:}CH\cdot CN$$

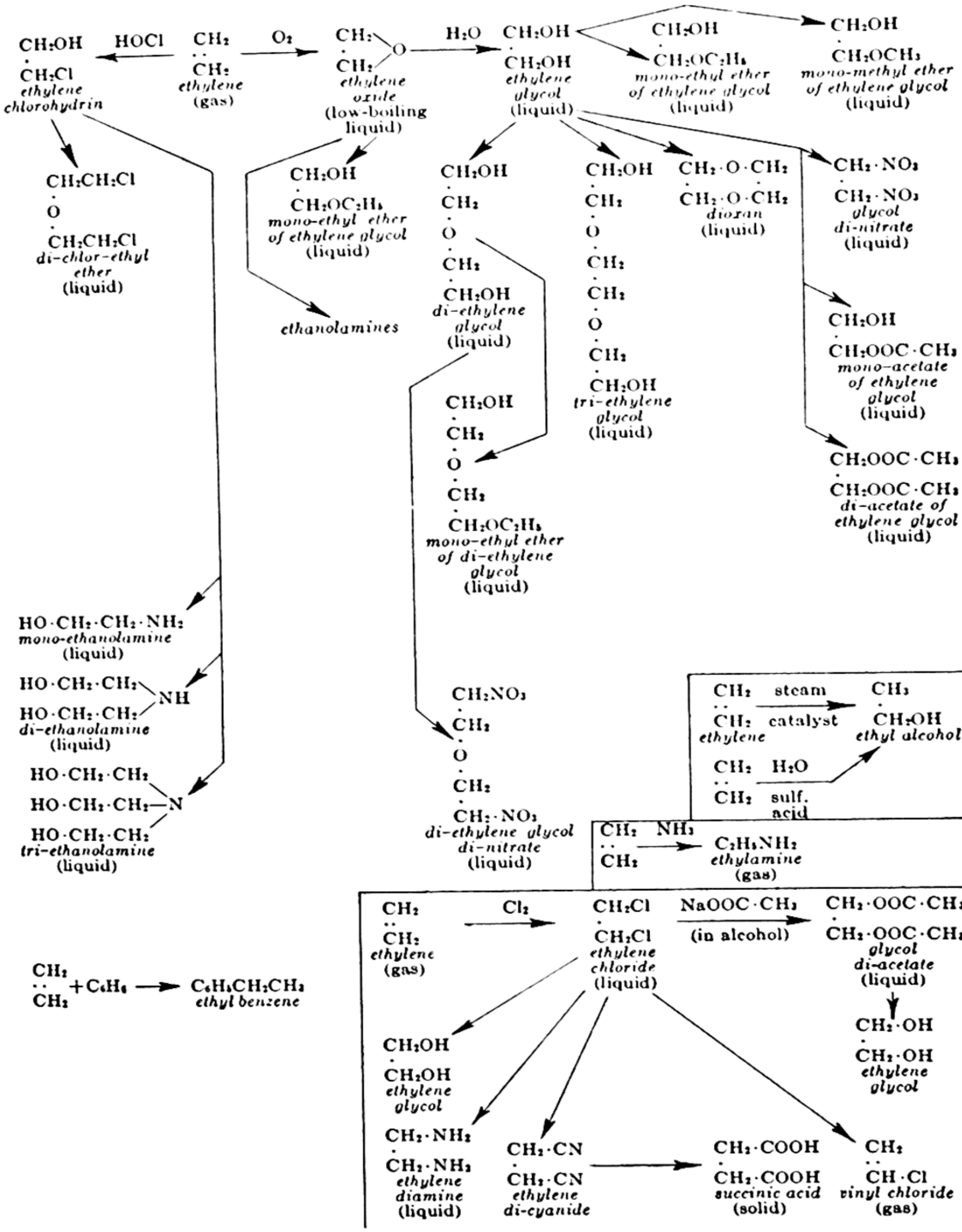
acrylonitrile (a liquid)

Synthetics with Ethylene (Ethene) as Starting Material

An important series of valuable organic compounds has been created, chiefly by the brilliant work of American chemists and chemical engineers, in building up derivatives of the molecule of ethylene or ethene ($CH_2{:}CH_2$). The "family tree" shown in Table 96 indicates the relation between the more important members of this series. Ethylene is an unsaturated compound which readily forms addition products. With oxygen, it forms ethylene oxide, which may be made to react with water to give the central substance of the series, ethylene glycol ($HO\cdot CH_2\cdot CH_2\cdot OH$) a liquid, manufactured at the rate of over 250 tons a day. Ethylene adds ammonia, hydrogen cyanide, water, hypochlorous acid, and chlorine. In the chlorinated derivatives, the halogen may be replaced by a hydroxyl (OH), an ethoxy (OC_2H_5) or other alkoxy group, or an acetyl radical ($OOC\cdot CH_3$). The same chlorinated derivatives may undergo reactions in which hydrogen chloride is removed, producing valuable derivatives with new properties. In alkylation, ethylene is added to selected hydrocarbons; finally, it is added to itself, to give us the prized soft plastic, polyethylene, or polythene.

[13] Consult the official reports cited. A valuable chart entitled Alkynol Synthesis with Formaldehyde appears on *Chem. Eng. News,* 25, 1040 (1947).

TABLE 96.—*Ethylene and some of its derivatives of commercial importance.*



Ethylene. Ethylene is a gas, and is obtained in the large amount required for the industries, depending upon its chemistry, from refinery gases, the off-gases, from cracked natural gas, or by thermal cracking of propane. It is also produced in the electric-arc cracking of natural gas for acetylene in substantial percentages. From all such gas mixtures, the ethylene must be concentrated to moderate purity for many purposes, and to high purity (95 to 99 per cent) for other processes, as for example, for making polyethylene or styrene. The raw gas may be compressed to several atmospheres and passed to a tower with shelves for solution in acetone[14] (see Figure 211). The acetone travels down, while the gas travels up. An

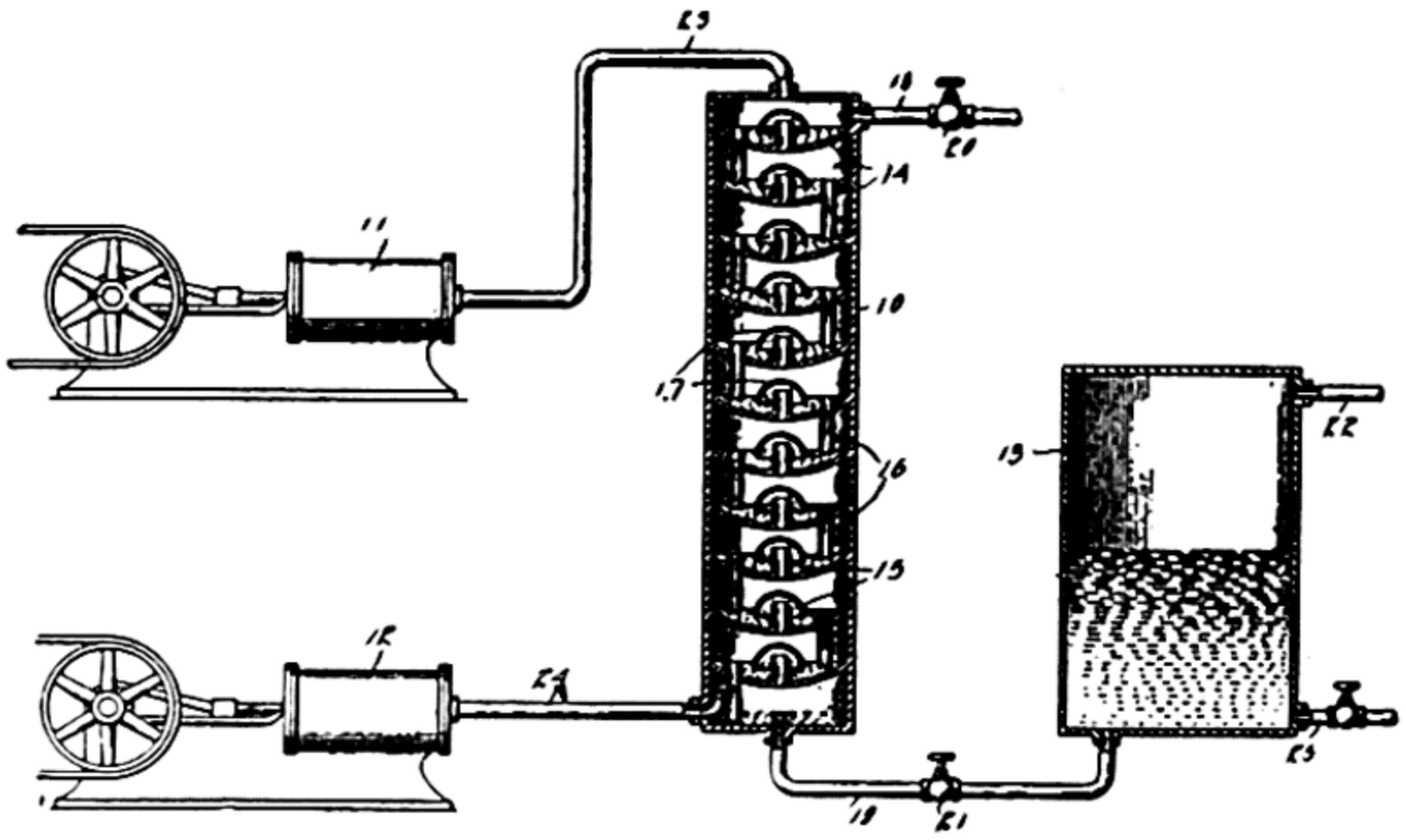


FIGURE 211.—Plant for the extraction of ethylene from a gas mixture, showing absorption tower, separating chamber, and the two compressors. (From the patent.)

acetone solution rich in ethylene collects at the bottom of the tower and is sent to an expansion chamber, where the pressure is released; the pure gas escapes from the liquid and is drawn off through a line at the top of the chamber. The liquid remaining is used over again, entering the absorption tower at its head. The pure ethylene gas is stored in a gas holder from which it is drawn as needed. Unabsorbed gases, such as hydrogen and methane, may be drawn from the upper section of the absorption tower.

The separation of the ethylene may be performed by liquefying it, allowing the non-condensables to escape, and refining the liquid portion by distillation in order to remove propane and higher hydrocarbons. Of late there has been developed the *hypersorption process* which functions in a single vertical unit with many sections. A continuous bed of granulated activated carbon travels slowly downward through a shell-and-tube exchanger, where it is cooled, then through an adsorption section in which it meets the gas and selectively adsorbs ethylene and the higher hydrocarbons. The activated carbon with its load of adsorbed components moves by gravity to the rectifying section, where it meets a reflux of heavy constituents and then steam; the ethylene is liberated and collected separately. The activated

[14] U. S. Pat. 1,422,184.

carbon continues down through a steaming section where the heavier components are liberated, to the outlet at the base of the tower, leading to a gas lift blower which elevates it to the top of the tower for another cycle. Methane and hydrogen are produced as a separate stream discharged near the top of the unit just under the heat exchanger. An example of the functioning of the hypersorption unit follows.

TABLE 97.—*Separation of ethylene in pilot plant operations* without sidecutting.*

Component	Feed	Make	Discharge
Methane	43.0	1.6	99.1
Ethylene	49.5	85.9	0.2
Ethane	5.5	9.3	0.4
Propane	2.0	3.2	0.3

* *Trans. Am. Inst. Chem. Eng.*, 42, 676 (1946).

A recovery of 98 per cent or better of the ethylene in the feed stream is usually obtained. The unit functions at the pressure level which fits in with the related processing operations; no compression is necessary, and no refrigeration.

A low-temperature fractionation process producing a 95 mole per cent of ethylene from 19.4 mole per cent of feed gas was described recently,[15] and also a fractionation system which avoids very low temperatures, but makes use of a liquid absorbent.[16]

The reported ethylene production in the United States for 1946 from petroleum sources was 294,605,000 pounds; production from alcohol and other non-petroleum sources was 12,889,000 pounds. In 1947, ethylene production had risen to 341,959,000 pounds. (Tariff Commission.)

Ethylene by the T P C process, from ethane to higher hydrocarbons, such as occurs in reduced crude petroleum, has been described in Chapter 24.

Ethylene Oxide. Ethylene oxide,[17] a gas at room temperature and a valuable intermediate, is made chiefly by the direct oxidation (with atmospheric air) of ethylene in the presence of a catalyst, such as finely divided silver on an alumina carrier. The presence of a small amount of water, such as would normally be present in the air, favors the reaction by repressing a side reaction given below. The proportions are one volume of ethylene to one volume of oxygen. The temperature in the reactor is between 150 and 400° C. (302 and 752° F.), generally 200° C. (392° F.), while the pressure may be near atmospheric, or as high as 100 lbs/sq in. The main reaction is

$$2\,CH_2{=}CH_2 + O_2 \rightarrow 2\,CH_2{<}\overset{}{O}{>}CH_2$$

ethylene *ethylene oxide*

[15] "Low-temperature processing of light hydrocarbons," A. W. Pratt and N. L. Foskett, *Trans. Am. Inst. Chem. Eng.*, 42, 149 (1946).

[16] "Ethylene purification by absorption process," Ludwig Kniel and W. H. Slager, *Chem. Eng. Progress*, 43, 335 (1947). Read also *Chem. Ind.*, 61, 205 (1947).

[17] U. S. Pat. 1,998,878; first reissue 20,370; second reissue 22,241.

A side reaction takes place to a small extent, in which carbon dioxide and water are formed:

$$C_2H_4+3O_2 \rightarrow 2H_2O+2CO_2.$$

On cooling the gaseous mixture leaving the reactor, ethylene oxide is condensed. Its boiling point when pure is 10.7° C. (51.6° F.). The process is continuous.

Ethylene Chlorohydrin. Ethylene forms an addition compound with hypochlorous acid in water solution

$$C_2H_4+HOCl \rightarrow HO\cdot CH_2\cdot CH_2\cdot OH.$$

The chlorohydrin formed also remains in solution. Inasmuch as hypochlorous acid is not stable, its sodium salt (NaCl) is prepared, and the free acid liberated only at the moment it is to react.[18] As the reaction is exothermic, cooling coils must be provided. By keeping the concentrations low, and circulating the liquor, the yield is improved.[19] In a continuous process (Reppe), chlorine mixed with a great excess of ethylene is pumped from below into one of several vertical reaction towers filled with water. Ethylene chlorohydrin is produced as an aqueous solution, and is withdrawn at a uniform rate, while an equivalent amount of water is added. The excess ethylene leaving the top of the tower is pumped in again, and provides excellent mixing. The temperature is held at 50° C. (122° F.). Ethylene chlorohydrin was for many years the main material for manufacturing ethylene glycol, which was done by reacting it with sodium bicarbonate in an ingenious apparatus.[20] It is still a valuable intermediate. Under certain circumstances, it may be made the source of ethylene oxide or of glycol.

Ethylene Glycol. The present main method of making ethylene glycol is the hydration of ethylene oxide:

$$\begin{array}{l} CH_2 \\ | \quad O \\ CH_2 \end{array} + H_2O \rightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

ethylene oxide *ethylene glycol*

The hydration may be performed in a closed vessel, with water made slightly alkaline. Ethylene oxide is soluble in water, and gradually hydrates. In the continuous pressure hydrolysis of Reppe, the reaction takes place without catalyst. In one process for the preparation of ethylene oxide from ethylene by oxidation, "the ethylene oxide issuing from the reaction vessel is sprayed with water to form the glycol derivative, and the undissolved gases pass out of the tower.[21]

The glycol solution may be concentrated by heating in a vacuum. When completely dehydrated it is a somewhat viscous liquid, very hygroscopic, boiling at 197.2° C. (387° F.). It is miscible with water in all proportions, causing a drop in the freezing point of the solution; 60 per cent ethylene

[18] U. S. Pat. 1,456,916.
[19] U. S. Pat. 1,456,959.
[20] U. S. Pat. 1,442,386.
[21] U. S. Pat. 2,367,169; see also 2,366,724.

glycol and 40 per cent water have the minimum freezing point, −49° C. (−56° F.); hence its value as an antifreeze in automobile radiators.

Ethylene glycol may also be made from ethylene chloride ($C_2H_4Cl_2$) in a single step,[22] or from glycol diacetate.[23] In a still more striking method which embodies much of the modern science of catalysis, formaldehyde is reacted with carbon monoxide and a molecule of water; the resulting hydroxy-acetic acid is esterified, and the methyl hydroxy-acetate hydrogenated, with formation of the desired glycol and regeneration of the methyl alcohol used in reaction (2).[24]

$$HCHO + CO + H_2O \xrightarrow[\text{catalyst}]{\text{high pressure}} \underset{\textit{hydroxy-acetic acid}}{CH_2(OH)COOH} \qquad (1)$$

$$CH_2(OH)COOH + CH_3OH \rightarrow CH_2(OH)COOCH_3 + H_2O \qquad (2)$$

$$CH_2(OH)COOCH_3 + 2H_2 \xrightarrow[\text{catalyst}]{\text{high pressure}} OH\cdot CH_2\cdot CH_2OH + CH_3OH \qquad (3)$$

The production of ethylene glycol in the United States in 1946 was 192,176,000 pounds; in 1947, it was 226,673,000 pounds (Tariff Commission).

Ethylene Chloride. Ethylene chloride is formed by passing ethylene gas into a cylindrical container in which a contact substance such as activated carbon has been placed. Chlorine enters at the same level, and the two gases travel downward; the liquid product is trapped in a separator.

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \text{ (liquid)}.$$

The gases may also be introduced into a body of liquid from previous batches, under a layer of water. The heat of formation of ethylene chloride by this reaction is considerable (60 calories per gram mole), and must be removed by cooling coils or a cooling jacket.

Oxo Process. In the Oxo process, ethylene and water gas are reacted catalytically to form propionaldehyde and diethyl ketone. Higher olefinic hydrocarbons containing C_{11} to C_{17} form under similar conditions the corresponding carbonyl compounds. In general the olefin molecule yields an oxygenated molecule higher in molecular weight by one carbon atom. The catalyst is cobalt, with thoria and magnesium carbonate as promoters, on kieselguhr, suspended in diesel oil. The pressures are of the order of 150 atm. and the temperatures as high as 180° C. The carbonyl compounds may be converted into corresponding alcohols, for example, by catalytic hydrogenation. The alcohols of the proper molecular weights may then be sulfated to produce one type of synthetic detergents.[25]

Glycol Esters. One of the earliest derivatives of ethylene glycol was the acetate ester, a substance which has good solvent properties; since then a number of other esters have been manufactured, but the ether-alcohols and the ether-esters, both to be presented in this chapter, have overshadowed the esters. The esters are important intermediate products between ethylene chloride and glycol, for example.

[22] U. S. Pat. 1,402,317.
[23] U. S. Pat. 1,454,604.
[24] *Chem. Ind.*, 61, 206 (1947).
[25] *Chem. Ind.*, 60, 232 (1947), with a flow sheet.

It may be noted that a mono-ester of a glycol is an alcohol ester, while the corresponding di-ester would have no alcohol group.

A satisfactory, inexpensive method [26] of forming ethylene glycol monoacetate consists in placing glycol and acetic acid in a boiling kettle (copper) with a vertical extension serving for refluxing a part of the vapors evolved. The temperature is maintained around 100° C. (212° F.); the water formed during esterification is able to escape through the refluxing jacket, while glycol, acetic acid or ester are re-condensed. Any water of dilution introduced with the acetic acid will also pass out, so that it is the special merit of this method that the ester may be produced with weak acetic acid such as 25 per cent acid, a cheaper material than 99 per cent or 99.8 per cent acid. The boiling is continued until the acid is essentially all combined:

$$OH\cdot CH_2\cdot CH_2\cdot OH + HOOC\cdot CH_3 \rightarrow \underset{\textit{ethylene glycol monoacetate}}{OH\cdot CH_2\cdot CH_2\cdot OOC\cdot CH_3} + H_2O.$$

The ester is purified by distilling it; any unchanged acid passes over first, and then the ester.

The diacetate is formed in the same way, except that twice the amount of acetic acid is placed in the kettle. The reaction then is:

$$OH\cdot CH_2\cdot CH_2\cdot OH + 2HOOC\cdot CH_3 \rightarrow CH_3\cdot COO\cdot CH_2\cdot CH_2\cdot OCC\cdot CH_3 + 2H_2O.$$

The diacetate may also be made from ethylene chloride, by heating it to 160° C. (320° F.) under pressure with sodium acetate and ethyl alcohol as a diluent.[27]

Glycol Nitrates. Ethylene glycol dinitrate is manufactured very much as nitroglycerin is, and it is used as an explosive. Its effectiveness as an explosive equals that of nitroglycerin; its great value is in the manufacture of low-freezing dynamites, as it freezes at − 22.8° C. (− 9° F.), while nitroglycerin freezes at + 13° C. (+ 55.4° F.). It is less sensitive to shock than nitroglycerin. Diethylene glycol may also be nitrated; the resulting dinitrate has the low freezing point of − 11.3° C. (+ 11.5° F.), and is used with ethylene glycol dinitrate in the manufacture of other low-freezing dynamites.

Glycol Ethers. The insistent demand for chemicals which would be good solvents for nitrocellulose stimulated the study of glycol derivatives. It was thought that the combination of the ether group with the alcohol group in a single molecule should confer superior solvent properties,[28] because the first solvent for nitrocellulose was an ether-alcohol mixture; neither of the substances alone had any solvent action. This expectation was fully and brilliantly realized. One of the first compounds of this type was the monoethyl ether of ethylene glycol ($OH\cdot CH_2\cdot CH_2\cdot OC_2H_5$) sold under the name of "Cellosolve."

A simple and efficient method for its preparation, in a single step, from inexpensive reagents, is as follows [29]: Ethylene glycol of commercial grade,

[26] U. S. Pat. 1,534,752.
[27] U. S. Patent 1,430,324.
[28] *Ind. Eng. Chem.*, 18, 700 (1926).
[29] U. S. Patent 1,614,883.

di-ethyl sulfate, and caustic soda (crushed solid) in the proportions required by the reaction:

$$2OH\cdot CH_2\cdot CH_2\cdot OH + 2NaOH + (C_2H_5)_2SO_4 \rightarrow 2OH\cdot CH_2\cdot CH_2\cdot OC_2H_5 + Na_2SO_4 + 2H_2O$$

are boiled in a kettle with reflux tower for 3 hours. After that time, the liquor is vacuum-distilled, leaving the inorganic salt in the still. The distillate is redistilled at atmospheric pressure and the recovery is 60 per cent or over. The product is a colorless liquid boiling at 134° C. (237° F.); it is soluble in water, glycerin, ethylene glycol, amyl acetate and butyl acetate. It is a solvent for gums, resins, and nitrocellulose; it has been proposed as an extraction agent for essential oils and for flavors and perfumes. This product is the monoethyl ether of ethylene glycol, with the ether oxygen binding the ethyl group to a carbon atom of the glycol group: $OH\cdot CH_2\cdot H_2C/O/C_2H_5$.

Another process [30] starts with ethylene oxide, and causes one molecule of ethyl alcohol to add itself to one molecule of the oxide:

$$\begin{matrix} CH_2 \\ CH_2 \end{matrix}:O + C_2H_5OH \rightarrow OH\cdot CH_2\cdot CH_2\cdot OC_2H_5.$$

Ethylene oxide, a liquid at room temperature only when under pressure, is pumped into an autoclave into which absolute ethyl alcohol has been placed, in the proportions indicated by the reaction and a 15 per cent excess of alcohol. The autoclave is then sealed and the temperature raised to 150° C. (302° F.) and kept there for 12 hours; or it may be heated to 200° C. (392° F.) and kept at that mark for 4 hours. At 150° C., the pressure rises to 250 pounds per square inch at the beginning of the reaction and toward the end falls to 125 pounds. The product is fractionally distilled to remove residual ethylene oxide and alcohol; the glycol ether passes over at around 134° C. (273° F.), leaving in the still the higher-boiling reaction products, such as the ethyl esters of di- and triethylene glycols which are formed to a certain extent. The yield is 70 per cent based on the alcohol reacted.

Other Glycol Derivatives. An ether-ester is formed by treating, for example, monoethyl ether of ethylene glycol with acetic acid in the same way the monoacetate ester of ethylene glycol is prepared. Such chemicals have proved of value as solvents.

The polyglycols and mixed polyglycols are formed by heating the glycol or mixed glycols with a moderate amount of phosphoric acid, or other dehydrating agent; they are also obtained as by-products in any reaction in which two glycol molecules might suffer dehydration. Several examples of such higher glycols are given in Table 98. The reader will please note that diethylene glycol has one ether oxygen in the molecule, and triethylene glycol two; their properties are therefore rather those of ether-alcohols, and do not closely resemble those of glycerin. Not only ethylene, but also propylene ($CH_3CH_2:CH_2$), butylene ($CH_3\cdot CH_2\cdot CH_2:CH_2$), and their isomers, lead to glycols, each one of which gives ethers, esters, and mixed ether-esters and

[30] U. S. Patent 1,696,874.

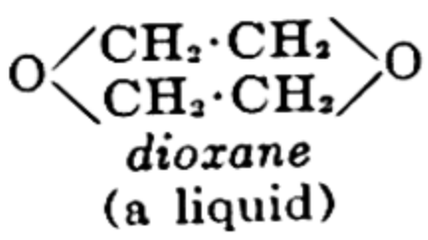
TABLE 98.—*Synthetic organic chemicals, mainly ethylene derivatives.**

Name	Formula	Sp. gr. 15°/15° C.	B.P. ° C. at 760 mm.	V.P. at 20° C. mm. Hg.
Acetic acid	$CH_3 . COOH$	1.049	118	....
Acetic anhydride	$CH_3 . CO . O . CO . CH_3$	1.082	140	....
Acetone	$CH_3 . CO . CH_3$	0.7972	56.2	186.3
Dichloroethyl ether	$CH_2Cl . CH_2OCH_2 . CH_2Cl$	1.230	178	0.73
Diethanolamine	$(C_2H_4OH)_2NH$	1.10	271° at 150 mm.	<0.01
Diethylene glycol	$CH_2OH . CH_2OCH_2 . CH_2OH$	1.1212	244.5	<0.01
Diethylene glycol ethyl ether or "Carbitol"	$CH_2OH . CH_2OCH_2 . CH_2OC_2H_5$	0.9996	198	0.13
Diethylene glycol butyl ether or "Butyl Carbitol"	$CH_2OH . CH_2OCH_2CH_2OC_4H_9$	0.940	222	0.05
Dioxane	$CH_2OCH_2 . CH_2OCH_2$ (ring)	1.0418	100.8	29
Ethyl alcohol (absolute)	$C_2H_5 . OH$	0.789	78	44
Ethyl ether	$C_2H_5 . O . C_2H_5$	0.719	34.5	425
Ethylene chlorhydrin	$CH_2OH . CH_2Cl$	1.213	128.7	4.9
Ethylene chlorhydrin 42.3 per cent	$CH_2OH . CH_2Cl$	1.0979	96	12
Ethylene diamine	$NH_2 . CH_2 . CH_2 . NH_2$	0.902	117	10.7
Ethylene dichloride	$CH_2 . Cl . CH_2Cl$	1.266	83.5	62
Ethylene glycol	$CH_2OH . CH_2OH$	1.1176	197.2	0.09
Ethylene glycol methyl ether or "Methyl Cellosolve"	$CH_2OH . CH_2OCH_3$	0.9748	124.5	7.5
Ethylene glycol ethyl ether or "Cellosolve"	$CH_2OH . CH_2OC_2H_5$	0.9360	134.8	4.6
Ethylene glycol butyl ether or "Butyl Cellosolve"	$CH_2OH . CH_2OC_4H_9$	0.9188	170.6	0.85
Ethylene glycol ethyl ether acetate or "Cellosolve acetate"	$CH_3COOCH_2 . CH_2OC_2H_5$	0.976	153	1.26
Ethylene oxide	$CH_2 . O . CH_2$ (ring)	0.887 at 7° C.	10.7	1095
Isopropanol 87.9 per cent	$CH_3 . CHOH . CH_3$	0.8229	80.3	35
Isopropyl ether	$(CH_3)_2CH . O . CH(CH_3)_2$	0.730	68.4	118
Methanol	CH_3OH	0.7965	64.7	95
Monoethanolamine	$(C_2H_4OH)NH_2$	1.018	171° at 150 mm.	0.5
Triethanolamine	$(C_2H_4OH)_3N$	1.12	277° at 150 mm.	<0.01
Triethylene glycol	$CH_2OH(CH_2OCH_2)_2CH_2OH$	1.120	278	<0.01

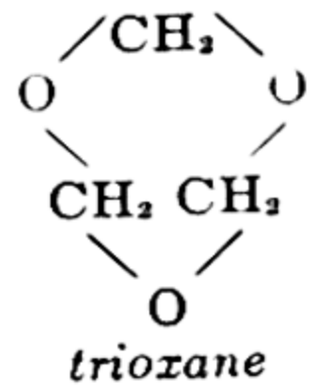
* In part, from the information bulletin issued by the Carbide and Carbon Chemicals Corporation, New York.

ether-alcohols which may have a special merit in some industrial application. For nitrocellulose and similar lacquer-forming substances, the ethylene glycol derivatives have about the right range of vapor pressure at medium and room temperatures.

Cyclic ethers of higher molecular weights are now commercial products, *e.g.*, dioxane, really 1,4-dioxane, and trioxane:



dioxane
(a liquid)



trioxane
(a solid)

obtained by distilling ethylene glycol with concentrated phosphoric acid, is of value as solvent. Of late, trioxane has been offered to the trade.[31]

A modified ammonia which is also an alcohol, has been formed by allowing ethylene chlorohydrin to react with ammonia; triethanolamine is the best known of the three possible modifications. (For properties, *see* Table 98.) It is of great value as an emulsifier; it forms with fatty acids soaps of unusual properties, and in other ways is finding wide application in the industries.[32] In another method, ethylene oxide is allowed to react with ammonia in an autoclave. The ethanolamines are viscous, hygroscopic liquids of very mild odor; they are organic bases of mild alkalinity, and combine with free fatty acids to form soaps which have solubilities different from those of metallic soaps.

Ethylene diamine is formed by heating ethylene chloride with aqua ammonia under pressure (autoclave). A continuous process has been devised,[33] and in addition, the formation of triamine essentially prevented by using 15 moles of NH_3 to 1 of $(CH_2)_2Cl_2$.

$$Cl\cdot CH_2\cdot CH_2\cdot Cl + 3NH_3 \rightarrow NH_4Cl + H_2N\cdot CH_2\cdot CH_2\cdot NH_2\cdot HCl$$

Dichloroethyl ether is formed by the removal of a molecule of water from two molecules of ethylene chlorohydrin.

Ethylene reacts with steam at 400° to 500° C. and 25 to 200 atm. pressure, in the presence of a dehydrating catalyst such as thoria, or phosphoric acid deposited on charcoal,[34] to form ethyl alcohol.

In Table 98, some additional information regarding the numerous ethylene and other olefin derivatives is given.

Nitroparaffins. A number of interesting synthetics which are paraffin derivatives made mainly by straight chemical reactions are now available commercially; they are useful in themselves, as medium-boiling, mild-odored solvents for resins and numerous other substances, and as starting materials for other substances. The new substances are nitroparaffins, nitromethane

[31] U. S. Pat. 2,304,080, to C. E. Frank 2,304,431 and 2,347,447 to J. F. Walker.
[32] *See* gas purification, Chapter 14.
[33] U. S. Patent 1,832,534.
[34] Brit. Patent 308,859, Jan. 1928.

TABLE 99.—*Nitro paraffins and their derivatives.**

		Molecular Weight	Sp. Gravity at 20° C./20° C.	Pounds per U. S. Gallon 68° F.	Boiling Point °C. Pure Compound
Nitromethane	CH_3NO_2	61.04	1.139	9.48	101.2
Nitroethane	$CH_3CH_2NO_2$	75.07	1.052	8.75	114.0
1-Nitropropane	$CH_3CH_2CH_2NO_2$	89.09	1.003	8.35	132.0
2-Nitropropane	$CH_3CHNO_2CH_3$	89.09	0.992	8.24	120.3
2-Nitro-1-butanol	$CH_3CH_2CHNO_2CH_2OH$	119.12	.....	....	105*
2-Nitro-2-ethyl-1,3-propanediol	$CH_2OHC(C_2H_5)NO_2CH_2OH$	149.15	.....	....	D
2-Nitro-2-methyl-1,3-propanediol	$CH_2OHC(CH_3)NO_2CH_2OH$	135.12	.....	....	D
2Nitro-2-methyl-1-propanol	$CH_3C(CH_3)NO_2CH_2OH$	119.12	.....	....	95*
1-Chloro-1-nitroethane	$CH_3CH(NO_2)Cl$	109.52	1.258	10.47	122–128.5
1-Chloro-1-nitropropane	$CH_3CH_2CH(NO_2)Cl$	123.54	1.209	10.06	139.5–143.3
2-Chloro-2-nitropropane	$CH_3CCl(NO_2)CH_3$	123.54	1.193	9.93	129–132.3
Diacetone, A.F.	$CH_3COCH_2C(CH_3)_2OH$	116.16	0.937–0.943	7.81	164–166
1,1-Dichloro-1-nitroethane	$CH_3C(NO_2)Cl_2$	143.97	1.405	11.69	122–125
1,1-Dichloro-1-nitropropane	$CH_3CH_2C(NO_2)Cl_2$	157.99	1.314	10.93	141–143.6

* From a list published by Commercial Solvents Corporation.

nitroethane, 1-nitropropane, 2-nitropropane, nitrohydroxy derivatives, and chloronitroparaffins. Hydroxylammonium salts are made from the nitroparaffins.[35]

Synthetic Methanol

It was in 1923 that a synthetic organic chemical in the form of thousands of gallons of methanol (or methyl alcohol, CH_3OH), which arrived in New York from Germany, created a sensation in the American industrial world.

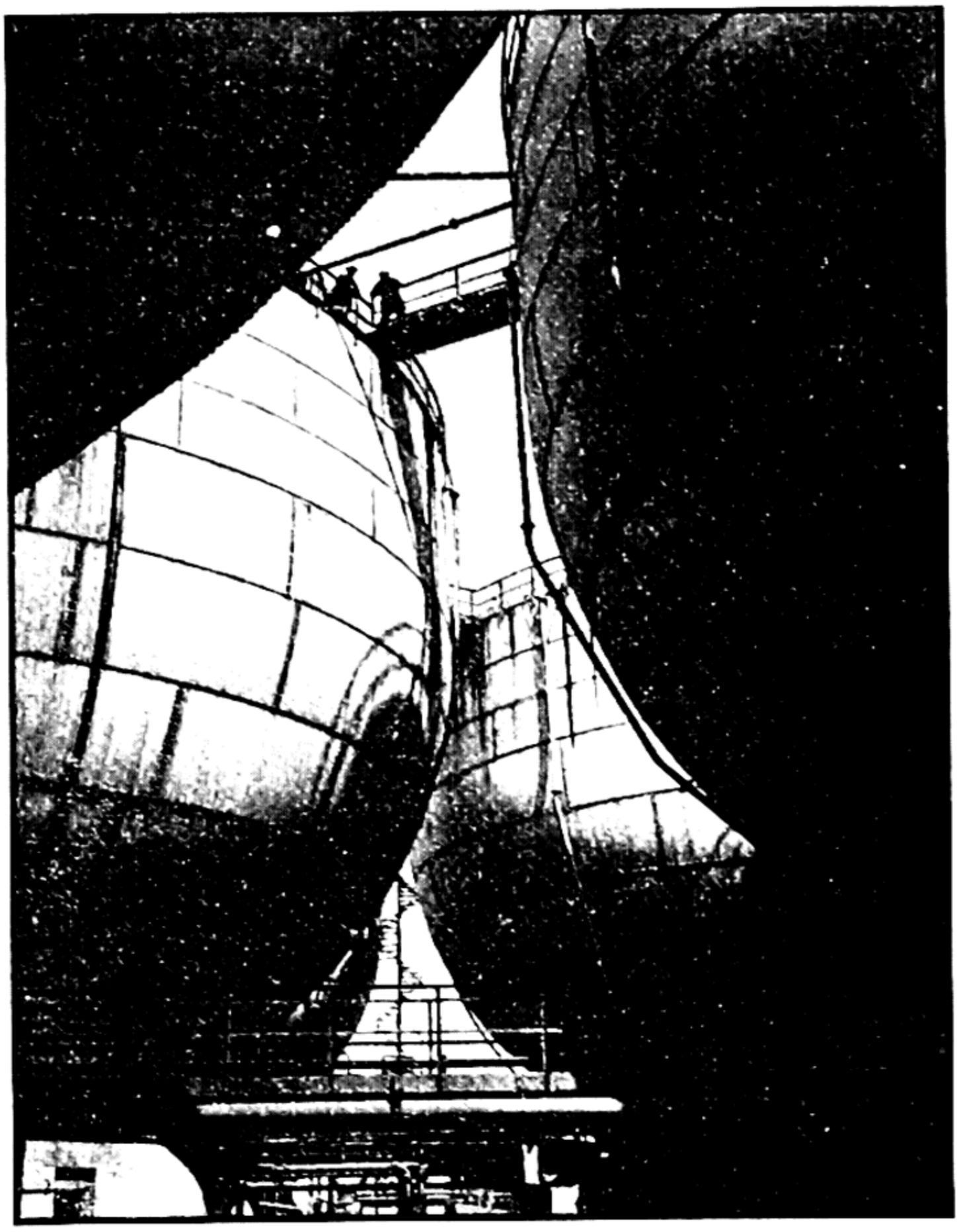


FIGURE 212.—Storage tanks for synthetic organic chemicals such as methanol, Leuna Works, formerly I. G. Farbenindustrie, Germany. (Bourke-White Photo, Pictures, Inc., N. Y.)

It was to be sold, duty paid, for 40 cents a gallon, a price about half that currently charged for methanol from wood. Since that time, plants synthesizing methanol from carbon monoxide and hydrogen have been erected in the United States, and have been most successfully operated. The reaction, which must be catalyzed, has even been applied to remove an impurity (CO) from hydrogen destined for direct ammonia synthesis. In 1947, the U. S. production of synthetic methanol was 555,481,000 pounds, about 10 per cent more than in the previous year. The production of natural methanol is in the range of 17 million pounds per year.

[35] A booklet may be obtained from the Commercial Solvents Corporation, 17 East 42nd street, New York.

The original catalyst [36] has been modified, and for many years zinc oxide with ten per cent chromium oxide [37] has been in successful use. The gas mixture is 70 parts hydrogen and 30 parts carbon monoxide. The reaction is: $CO+2H_2 \rightarrow CH_3OH$. The effect of temperature and pressure on the conversion is indicated in Table 100.

TABLE 100.—*Percentage methanol at equilibrium ratio $H_2/CO=2$.*

Temp. ° C.	Pressure (atm. absolute) 1	10	50	100	300	600	1000
200	0.32	28.10	58.40	71.95	85.62	90.70	93.40
300	...	0.25	5.47	15.62	43.05	59.80	69.80
350	...	0.04	1.02	3.69	19.51	37.11	50.46
440	...	...	0.20	0.85	6.35	17.30	29.80
500	...	...	...	0.07	0.61	2.34	5.80
600	...	...	...	...	0.09	0.37	1.02

The converter is made of copper-lined nickel steel. The effect of space velocity on the conversion is indicated in Table 101. In general, the temperature employed is 350° C. (662° F.), the pressure 200 atm., though it may be anywhere between 50 and 1000 atm.

TABLE 101.—*Methanol conversion at 400° C. (752° F.).**

Gas mixture	Space velocity	Pressure Atm.	Conversion Per cent
$CO + 5H_2$	500	150	22.5
$CO + 2.7H_2$	625	204	26
$CO + 2H_2$	3000	180	19.5
$CO + 2H_2$	7500	180	16.8

* *Ind. Eng. Chem.*, 20, 1111 (1928).

The gases leaving the converter give up part of their heat to the incoming cold gas in heat exchangers, and are cooled further by water. The methanol condenses, with a conversion which may be, for example, 20 per cent; the unreacted gases are recycled. The synthesis is exothermic, furnishing enough heat to run the process without outside heat except when starting.

The problem is somewhat different when the reaction is to serve for the removal of a small percentage of carbon monoxide, such as 3 per cent, from a hydrogen gas. It is necessary to have a highly active catalyst, so that this small amount of carbon monoxide may be completely transformed into methanol. Such a catalyst is obtained [38] by melting together pure copper oxide and any oxide of chromium, titanium, molybdenum, zinc, or manganese, breaking up the resulting melt into fragments, and reducing these in hydrogen at 250° to 350° C. (482° to 662° F.). The copper oxide suffers reduction, leaving the metal; the other oxide is unreduced. The granules produced by this method are hard, highly porous, and very reactive at relatively low

[36] The original catalyst was 90 parts copper oxide with 10 parts zinc oxide, used by Patard; for the early history of the methanol developments, see *Ind. Eng. Chem.*, 17, 430 (1925); also Brit. Patent 229,715 to a Badische Anilin und Soda Fabrik correspondent, reproduced in *Ind. Eng. Chem.*, 17, 981 (1925). *See also* p. 859, same journal and volume.

[37] The Mittasch patent, U. S. Patent 1,558,559.

[38] U. S. Patents 1,844,857 and 1,844,129.

temperatures. The efficiency of this catalyst is high. The metallic copper tends to dissipate the heat of reaction and thus favor its progress, with the formation of more methanol. Pressures of 200 to 300 atm. are suitable, but at 1000 atm. the reaction proceeds smoothly.

The reaction between carbon monoxide and hydrogen may be directed by the choice of the catalyst. Thus, water gas passed at atmospheric pressure over nickel held at a temperature of 380° C. (716° F.) produces methane and carbon dioxide, and not methanol:

$$2CO + 2H_2 \xrightarrow{Ni} CH_4 + CO_2$$

With the volumes adjusted so that to 1 volume of carbon monoxide there are 3 volumes of hydrogen, the reaction goes practically to completion at the temperature of 230 to 250° C. (446 to 482° F.).

The effort to direct the reaction has been studied intensively by those in charge of developing the synthetic liquid fuel and chemicals process—the modified Fischer-Tropsch (see Chapter 24). The substances produced in that process are truly synthetic organic chemicals, if they are isolated as single chemical species and purified to the point of commercial purity. They include methyl and ethyl alcohol, aldehydes, acids, esters, ethers, ketones, hydrocarbons and cyclic compounds.

A number of catalysts and their functions are given in Table 102.

TABLE 102.—*Some catalysts and their uses.**

Reaction	Process	Catalyst
Hydrogenation	Methanol synthesis	Zinc oxide with chromium oxide, v.p.†
		Zinc chromite, v.p.
	Esters to alcohols	Copper chromite
	Vegetable oils to fats	Nickel, l.p.
	Acetylene to ethylene	Palladium
Dehydrogenation	Butylene to butadiene	Iron oxide on a magnesia base with CuO and K_2O in small amounts as promoters
	Ethyl benzene to styrene	
Hydration	Acetylene to acetaldehyde	Mercuric sulfate, l.p.
Dehydration	Dehydration of alcohols	Alumina
Polymerization	GR-S	Organic peroxides, l.p.
Alkylation	Ethyl benzene from ethylene and benzene	Anhydrous hydrofluoric acid
		Sulfuric acid
Oxidation, controlled	Benzene to maleic anhydride	Vanadium pentoxide, v.p.
	Naphthalene to phthalic anhydride	Vanadium pentoxide, v.p.
	Methyl alcohol to formaldehyde	Copper metal, v.p.
		Iron molybdate, v.p.
	Ethylene to ethylene oxide	Silver, g.p.
	Sulfur dioxide to trioxide	Vanadium pentoxide, platinum, g.p.
Decarbonylation	Furfural to furan	Iron chromite, short rods

* In part from "Catalyst manufacture: a growing industry," Earl C. Ray, *Chem. Eng.*, p. 127 (May, 1948).

† The notation v.p. stands for vapor phase, g.p. for gas phase, l.p. for liquid phase

Catalysts

Choice of Catalyst. The catalyst may be chosen for its ability to direct a reaction or for its greater reactivity, in order to bring about the reaction of a highly diluted impurity. An example of both of these purposes has been given in the preceding section.

Another instance of the directive influence of a catalyst is the following: with carbon monoxide-hydrogen gas zinc and copper chromite granules give mostly methanol; but if carried on alumina, or if mixed with granules of alumina, they give mainly dimethyl ether.

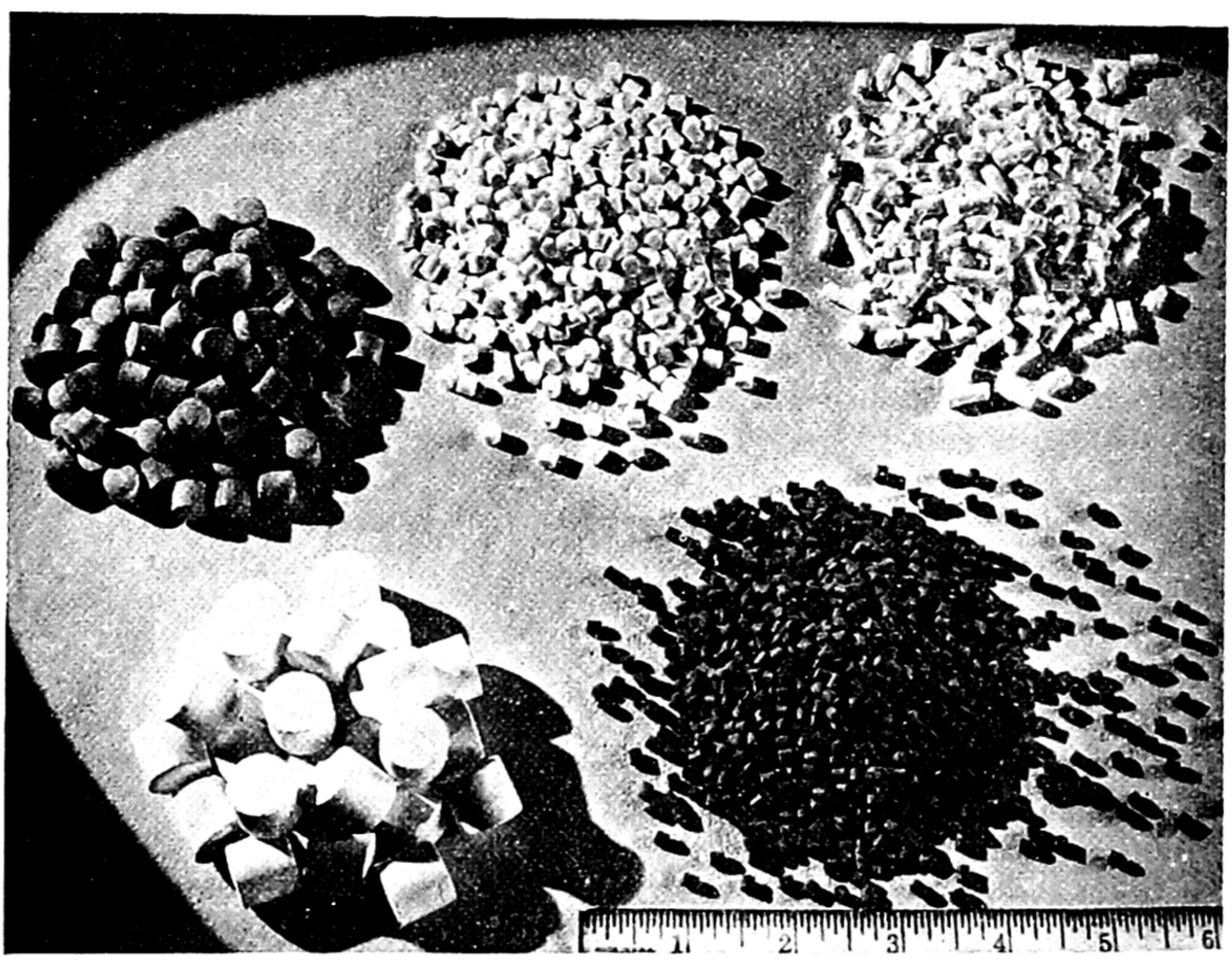


Figure 213.—Photograph of various pelletted and extruded catalysts, with a scale. (Courtesy of Harshaw Chemical Company, Cleveland, Ohio.)

The catalyst may also be chosen for its resistance to the deactivating action of an impurity. An example is as follows: The original discoverer of catalytic hydrogenation, such as that of hydrocarbons in the vapor phase, employed metallic nickel, especially at ordinary pressures. Nickel, cobalt, iron, copper and platinum are used chiefly to hydrogenate vegetable oils for the production of edible and non-edible vegetable fats. Nickel, however, is sensitive to impurities—so much so that the hydrogen must be absolutely pure, and the material to be hydrogenated must not contain any elements (impurities), which might adversely affect it. Hydrogenations are performed, however, upon bodies which are not pure, containing, for example, sulfur (petroleum fractions). Fortunately a number of oxides were found

that can resist impurities and are also excellent hydrogenating catalysts, *e.g.*, the oxides of molybdenum, tungsten, manganese, vanadium and chromium, with alumina, magnesia, zinc oxide, and potassium carbonate as promoting agents, used in very small amounts.

The conversion may differ with two catalysts, both of which are active. For example, in the decomposition of formamide to give hydrogen cyanide,

$$HCONH_2 \rightarrow HCN + H_2O$$

charcoal brings about a 72 per cent conversion, aluminum 96 per cent.

The catalyst is so chosen that it hastens the reaction and does not favor the formation of other products. The composition of the catalyst and the method for its preparation, its shape, as well as the conditions of temperature and pressure which are most advantageous, must be determined by experimentation, supplemented by previous experience.

The catalytically active agent may be "carried" on an inert material or base, such as small balls of refractory alumina so fabricated that they offer a great surface ("Alfrax") or fibers like asbestos. Both these carriers, it will be observed, are at the same time suitable for high-temperature work.

Manufacture of Catalysts. The manufacture of catalysts has become a large industry. If those used for cracking petroleum fractions are included, the summary given in Table 103 applies.

TABLE 103.—*Estimate of major catalyst replacements in 1948.**

Purpose	Catalyst	Short tons	Value
Synthetic cracking all kinds	Silica-alumina	38,000	$10,000,000
Hydroforming	Alumina	1,800	3,200,000
Dehydrogenation for butadiene	Various	410	600,000
Fat hydrogenation	Nickel	75	250,000

* From "Catalyst manufacture: a growing industry," Earl C. Ray, *Chem. Eng.* (1948). The table does not include catalysts used in the manufacture of ammonia, methanol and styrene. The prices for preformed and prepared catalysts range from $0.12 to 1.65 per lb.

The sizes and shapes of various solid catalysts appear in Fig. 213. The method for the manufacture[39] of the short cylinders is to prepare the original mix, which will generally be wet, and to place the mass, while still plastic, in an extrusion machine, provided with a multi-opening die such as shown in Fig. 214. The knife travels a circle and returns to cut off the short cylinder just as these reach the proper height. The cylinders are dried, perhaps roasted, and activated as indicated by preliminary study or by the regular practice.

Catalytic Pressures. A distinction is made between atmospheric, or low-pressure, catalysis and high-pressure catalysis.[40] As one would expect, the first work of Sabatier was at low pressures, and only subsequently was the field of high-pressure catalysis developed. Differently constructed equip-

[39] A flow sheet for the production of water gas conversion catalyst will be found in *Chem. Eng. Progress*, **44**, 369 (1948), and a layout of the same plant on p. 371. The water conversion reaction is $CO + H_2O \rightarrow CO_2 + H_2$.

[40] *See* "Catalysis, Inorganic and Organic," by Berkman, Morrell, and Egloff, New York, Reinhold Publishing Corp., 1940.

ment had to be devised, of materials able to withstand high pressures and elevated temperatures, and the accelerated chemical activities on container walls. A vast amount of information on the compressibility of gases and gas mixtures, on the flow of compressed gases through narrow bores, and on chemical equilibria, had to be obtained, before the present state of development was reached. The application of catalytic reactions to industrial processes has progressed well, and it will continue.

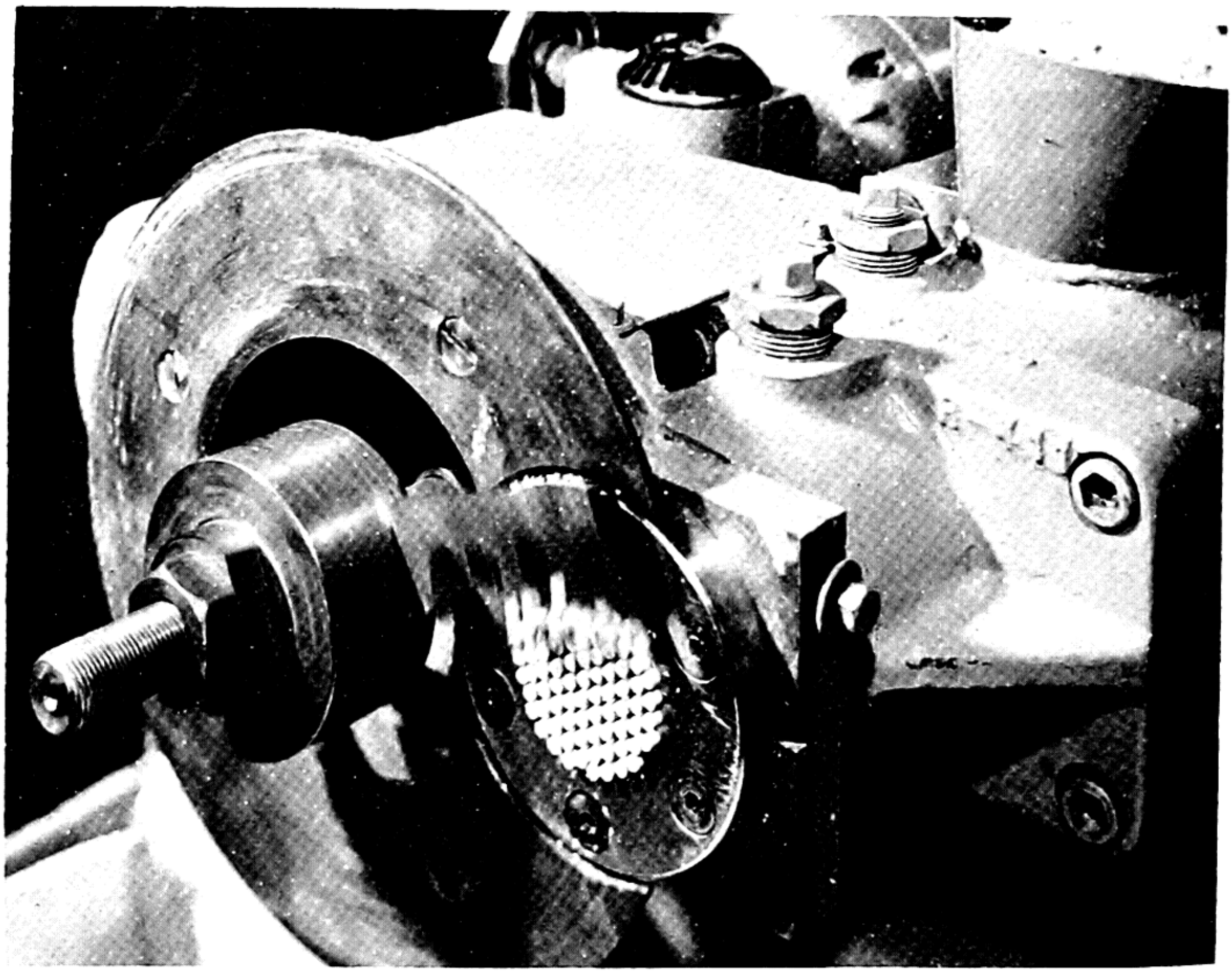


FIGURE 214.—An extrusion press which forms the short cylinder preforms of catalyst mass. The cylinders are dried, roasted, and activated. (Courtesy of Houdry Process Corporation, Philadelphia, Pa.)

It was formerly held that a catalytic agent accelerated a reaction which was slow, but could take place of itself. It is well to modify this in two respects, and to say: A catalyst hastens a slow, or even very slow chemical change, which, however, must be thermodynamically possible, and, when several products are obtainable, the catalyst is capable of directing the reaction.

Any substance which accelerates a reaction is a catalyst; it may be a substance dissolved in a liquid in which gases must in their turn dissolve, such as the violet acid in the sulfuric acid-nitric oxide chambers, or the hydrogen chloride and tin compounds in some of the hydrogenations of tars and coal to give motor fuels. The contact catalyst is frequently a solid, which is exposed to the gases, vapors, or to the liquid in which the reaction

TABLE 104.—*Some catalytic reactions of industrial importance.*

Reaction	Catalyst	Temperature ° C.	Pressure Atm.	Heat effect	Cal.
$2CO + 2H_2 = CH_4 + CO_2$	Ni	380	1	exothermic	60 *
$CO + 3H_2 = CH_4 + H_2O$	Ni	240	1	exothermic	
$CO + H_2O = CO_2 + H_2$	Fe	500	1	exothermic	10 *
$CO_2 + 4H_2 = CH_4 + 2H_2O$					
$CO_2 + CH_4 = 2CO + 2H_2$	$Ni + Al_2O_3$	900	1		
$CO + H_2$ = synthin	$Co + Cr_2O_3$	270	1		
$CO + 2H_2 = CH_3OH$	$ZnO + 10\%\ Cr_2O_3$ {lumps or granules}	350	200	exothermic	24 *
$CO + 2H_2 = CH_3OH$	Cu	350	200	exothermic	
$CO_2 + 3H_2 = CH_3OH + H_2O$	$ZnO + 10\%\ Cr_2O_3$	350	200	exothermic	14 *
$CO + H_2$ = synthol	$Fe + K_2CO_3$	400–450	100		
Coal + H_2	none (Bergius)	400	100		
Coal + H_2	Mo_2O_3 on Al_2O_3				
Min. oils + H_2	Mo_2O_3 on Al_2O_3		245	exothermic	
$C_2H_2 + H_2O = CH_3CHO$	$HgSO_4$	68	1	exothermic	28.14 *
$CH_3CHO + \frac{1}{2}O_2 = CH_3COOH$	$MnSO_4$	25	2–3	exothermic	56.6 *
$N_2 + 3H_2 = 2NH_3$	Fe granules with double promoter (American)	475	300	exothermic	11.89 †
$4NH_3 + 5O_2 = 4NO + 6H_2O$	Pt gauze	1025	1–3	exothermic	214.2 *
$SO_2 + \frac{1}{2}O_2 = SO_3$	Pt; or V_2O_5	500	1	exothermic	22.6 *

* Calories (large) evolved for the reaction as written; † for 17 grams of ammonia. Exothermic means with evolution of sensible heat to the outside; the chemical system involved loses the corresponding amount of heat, and is therefore written with a minus sign in thermodynamics.

is to take place; the solid may be in lump form, or powder; it may be by itself, or it may be supported on a "carrier," which is inert.

In the language of chemical kinetics, the catalyst works to overcome the energy of activation, which must be furnished to the molecule before it can react. The catalyst does not displace the equilibrium; it raises the rate (of the reaction) at which the equilibrium is attained, or approached.

The activity of, let us say, a metal surface in the case of hydrogenation is due to the surface of the metal. A comparatively small number of the surface atoms project into space, and are unbalanced with respect to their chemical affinities or valence. (*See* Fig. 215.) These projecting atoms form intermediate compounds, or complexes with the hydrogen; the forces involved are not distinguishable from the common chemical forces. If such an active center, or a near-by one, can also attract the second reactant,

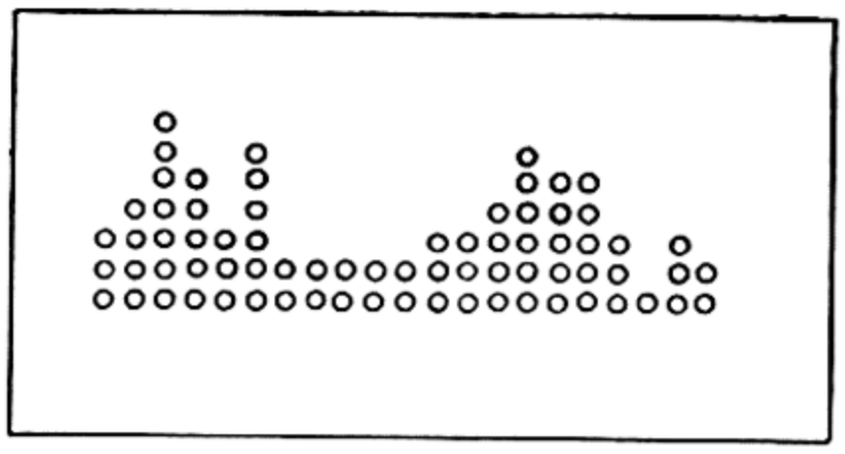


FIGURE 215.—The surface of metallic nickel, greatly enlarged to show the catalytically active centers formed by protruding atoms. (After Taylor.)

such as carbon monoxide, similarly distorting its normal structure, the two substances can meet while in the active state, and readily form a new grouping. Questions of adsorption are of primary importance. Adsorption may work for evil as well as good, however; in some cases adsorption stops the process. For example, 3 per cent carbon monoxide in hydrogen will retard ammonia formation, because the monoxide is adsorbed by the surface, thus preventing the approach of the hydrogen. The monoxide is then spoken of as a poison. According to this theory of catalytic mechanism "promoters" are considered to be substances which distort the crystal lattice in the catalyst still more than it normally is; in other cases, these promoters would be able to form the temporary complexes with the reactants which are necessary for the rapid change.

Loss of Efficiency. There are two ways in which a catalyst may lose its efficiency; one is by heat, the other by poisoning. The effect of excessive heat is to close, by fusion, the pores and micropores of the catalyst mass, thus destroying its surface for practical purposes by reducing it to an impotent minimum. A temporary inactivation results from the coating of the surface of the catalyst by a deposit of a solid or semi-solid, which blocks the way of the reactants. Such fouling occurs in petroleum cracking; it may be removed at regular intervals by burning off the deposit, thus restoring activity. "Poisoning" is the reduction of catalyst surface by a substance which is adsorbed and thus veils the active surface.

The rôle of temperature within the safe limit will be a compromise between two or more effects; it must not be so high that the adsorbed atoms and molecules are driven off so fast that no or little reaction can take place; yet it must be high enough so that the activation of the reactant molecules

is a maximum, and that very little additional force at the contact surface will suffice to form the adsorption complex.[41]

A figure in constant use in catalytic reaction studies is the space-velocity, by which is meant the volume of reacting gases passing over one liter of catalytic mass per hour. The volume in question is the volume of the exit gases, calculated to normal conditions of temperature and pressure, while the volume of catalytic mass is the volume occupied by the mass as spread out or packed in the reaction vessel.

It might be well to observe that the term "conversion" applies to a one-pass system. The term "yield," however, applies to a one- or a many-pass system, whichever is the practice.

The greater number of catalytic reactions presented in these chapters are heterogeneous, that is, involve two or more phases, such as solid and gas, or solid, liquid and gas. A homogeneous catalytic reaction would be the inversion of sucrose in solution by a dissolved acid. A heterogeneous catalytic reaction involving three phases is the hydrogenation of edible oils, in which hydrogen (gas), the oil (liquid) and the contact substance, nickel (solid), participate.

Hydrogenation and Controlled Oxidation

Among the most important catalytic reactions which produce organic chemicals—semi-synthetic if not synthetic—are the hydrogenation of a hydrocarbon obtained from natural sources, such as naphthalene or benzene, and the partial oxidation of the same or similar substances. Examples follow.

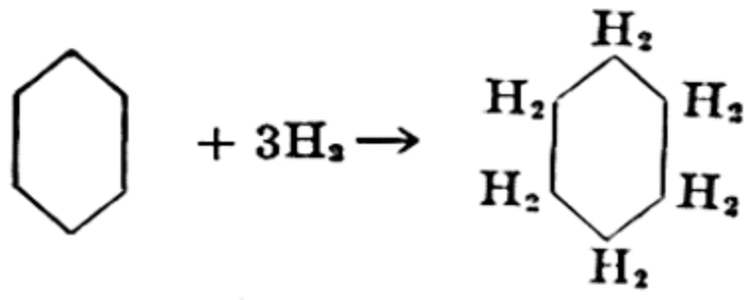
Naphthalene having nickel powder suspended in it may be melted in a pressure vessel with a stirrer, very much as is done in the hydrogenation of edible oils. At temperatures of 140 to 160° C. (284 to 320° F.), hydrogen is forced in under a pressure of 30 atm. Tetralin, a liquid boiling at 205° to 207° C. (401 to 405° F.), is formed; it is of value as a solvent and special blending agent. On long-continued hydrogenation, of less industrial importance, decalin is obtained.

$$C_{10}H_8 + 5H_2 \rightarrow C_{10}H_{18}$$
decalin (a liquid)

$$C_{10}H_8 + 2H_2 \rightarrow C_{10}H_{12}$$
naphthalene — *tetralin* (a liquid)

Naphthalene may be hydrogenated in the vapor phase, by passing naphthalene vapors mixed with hydrogen (pure) over nickel. Tetralin is formed.

Benzene vapors mixed with hydrogen and held over nickel at 140° C. (284° F.) give cyclohexane ($C_6H_6 + 3H_2 \rightarrow C_6H_{12}$, a liquid). Expressed graphically:



Phenol by a similar procedure gives cyclohexanol.

[41] For the theory of the mechanism of catalytic processes, see "Eighth report of the committee on contact catalysis," J. C. W. Frazer, *J. Phys. Chem.*, 34, 2155 (1930).

Phthalic Anhydride. By controlling the oxidation by air of naphthalene, a good yield of phthalic anhydride may be obtained; the catalyst is vanadium pentoxide, at an elevated temperature. By controlling is meant arresting it at a certain stage, for should it be allowed to proceed unchecked, only carbon dioxide and water would be the products.

In the most successful of the commercial installations,[42] air and naphthalene vapors from boiling naphthalene are thoroughly mixed in a hot mixing chamber, and passed over the catalyst in numerous square tubes, kept at about 357° C. (674.6° F.), in a downward direction. Figure 216 will

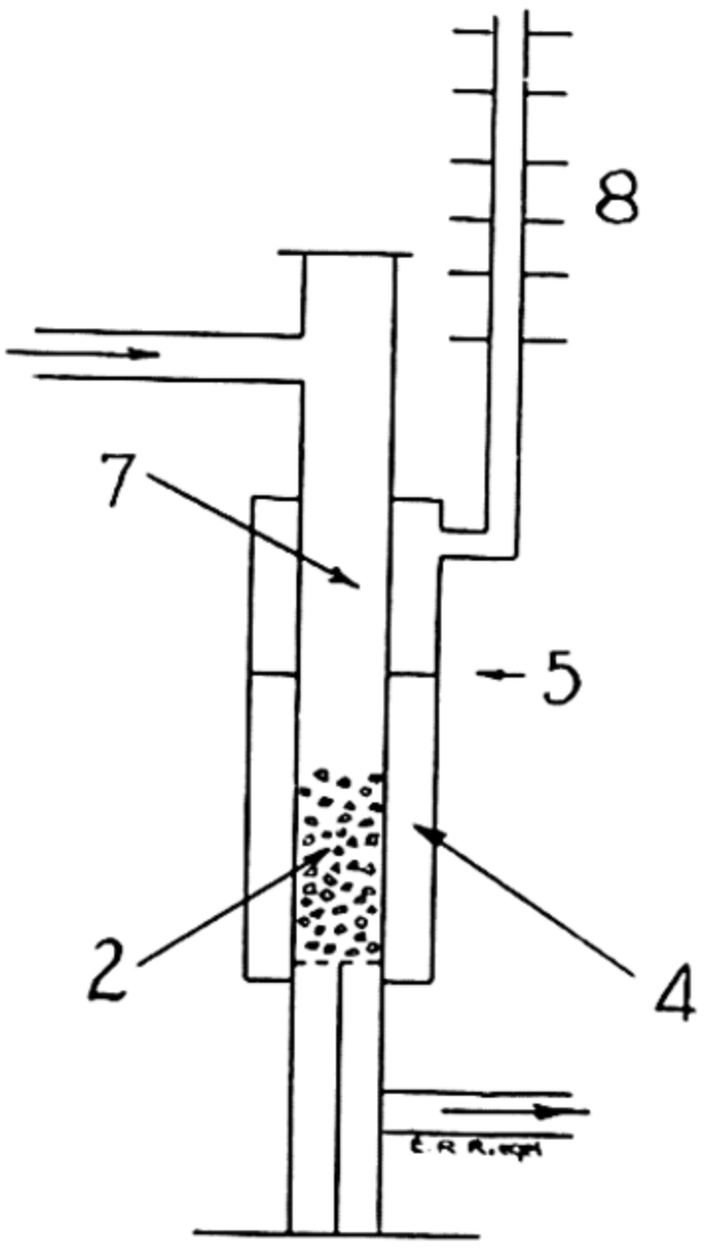
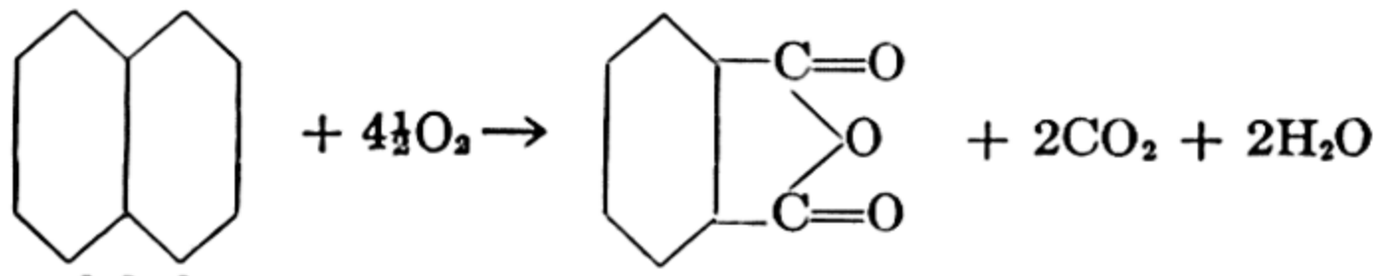


FIGURE 216.—Air-hydrocarbon oxidation. Single tube, with catalyst mass 2; level of mercury in the jacket 5; total condenser for the mercury 8; preheating part of reaction tube 7. In the full size installation, a nest of tubes is used.

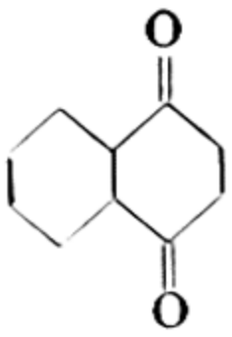
illustrate the disposition. Around the tubes a small body of liquid mercury is gently boiling. The converter consists of a nest of such tubes set in mercury, the whole surrounded by an outside jacket; the latter carries a vertical tube with fins which acts as an efficient condenser for the mercury. As the hydrocarbon and air react (on the surface of the vanadium pentoxide), much heat is evolved; it passes through the wall of the square tube to the mercury, which consumes it by vaporizing. In that way, the temperature is maintained near the boiling point of mercury, 357° C. (674.6° F.). The upper half of the catalyst tube is empty, and this part becomes the preheater for the incoming gases, which are already at an elevated temperature. The main reaction is:



naphthalene (white solid) — *phthalic anhydride* (white solid)

[42] U. S. Patent 1,374,720; for the basic patent of Gibbs, *see* U. S. Patent 1,285,117. *See also* U. S. Patent 1,444,068. In 1930, the Gibbs patent was cancelled, and U. S. Patent 1,787,417 and 1,787,416 were issued to Alfred Wohl, for the same process. These were attacked in court by the government, but in 1934, the Wohl patents were upheld and declared valid (see Chapter 40).

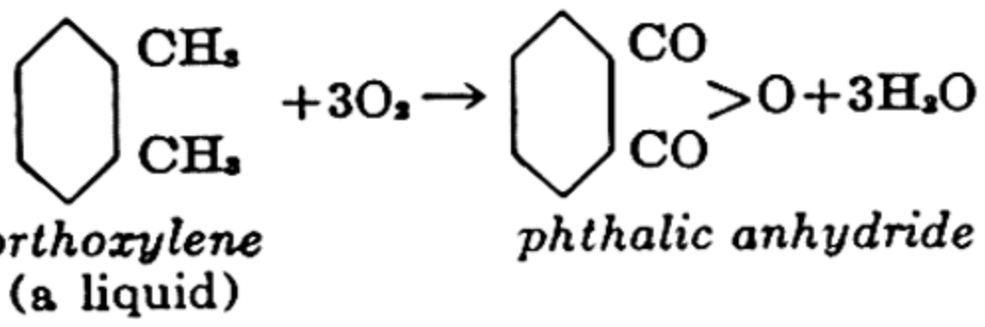
To a certain extent, benzoic acid, $C_6H_5 . COOH$, and naphthaquinone,



are formed, and are collected with the anhydride, while the gases pass out. A 72 per cent recovery of phthalic anhydride is feasible; it is isolated by sublimation or distillation, and is put on the market in the form of flakes.

In the original installations, the catalyst was made by dipping asbestos fibers into ammonium vanadate, and activated by passing hot air through it; instead of asbestos, pumice may be used. The square tubes are used as catalyst carriers because the ratio of surface to content is greater for a square tube than for a round one of same height and same cubical content. It should be noted that this oxidation is performed at atmospheric pressure. The temperature may be varied by operating under slightly higher pressures. Instead of mercury, liquid sulfur may be used.[43]

Supplementing naphthalene as raw material, and especially welcome in the Far West where there is no coal distillation, is orthoxylene,[44] a petrochemical separated from hydroformed stock. Orthoxylene is partially oxidized with air, by the agency of vanadium pentoxide, according to the reaction:

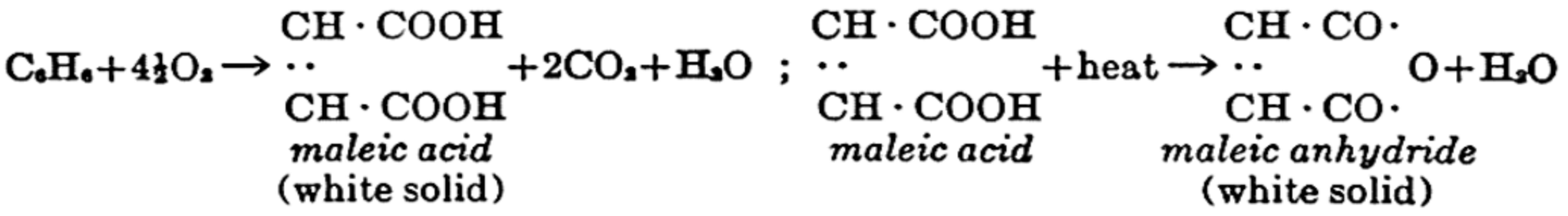


orthoxylene (a liquid) — *phthalic anhydride*

The catalyst is held in tubes of small diameter; the tubes are surrounded by molten salt, the heat transfer agent, which is rapidly circulated through the heating tubes of a steam boiler, and thus effectively removes the high heat of reaction. The product is collected in large condenser boxes. The crude is distilled in a packed tower under vacuum then again in a bubble cap tower also under vacuum, from which latter a "heart cut" of pure anhydride is taken. The anhydride is flaked on water-cooled aluminum drums.

The production of phthalic anhydride by catalytic oxidation in the United States was 112,746,000 pounds in 1946, valued at 13 cents a pound. In 1947, the production was 137,467,000 pounds, and the unit value 16 cents. (Tariff Commission.)

Maleic Acid. In the same apparatus serving for phthalic anhydride production, maleic acid is formed by the oxidation of benzene at a slightly higher temperature. A recovery of 60 per cent is considered good.



maleic acid (white solid) — *maleic acid* — *maleic anhydride* (white solid)

[43] U. S. Patent 1,547,167.

[44] "Phthalic anhydride manufacture from orthoxylene," L. E. Levine, *Chem. Eng. Progress*, 43, 168 (1947).

Maleic acid may be hydrogenated to succinic acid, or hydrated to malic acid; the latter is a substitute for citric acid in beverages. The esters formed from these acids in the standard way are valuable for their odor and solvent properties.

$$\begin{matrix} CH\cdot COOH \\ \dot{\dot{C}}H\cdot COOH \end{matrix} + H_2 = \begin{matrix} CH_2\cdot COOH \\ CH_2\cdot \dot{C}OOH \end{matrix}$$
succinic acid
(white solid)

;

$$\begin{matrix} CH\cdot COOH \\ \dot{\dot{C}}H\cdot COOH \end{matrix} + H_2O = \begin{matrix} CH(OH)\cdot COOH \\ \dot{C}H_2\cdot COOH \end{matrix}$$
malic acid
(white solid)

The United States sales of maleic acid and anhydride in 1945 were 7,759,000 pounds, valued at 25 cents a pound.

A method for purifying anthracene $C_{14}H_{10}$ of carbazol ($C_{12}H_9N$) by the selective catalytic oxidation of the latter has been described.[45]

Table 105 summarizes the reactions discussed and related ones.

TABLE 105.—*Hydrogenation and oxidation of natural organic compounds.*

Compound	Catalyst	Temp. °C.	Pressure Atm.	Product
Naphthalene + $2H_2$	Ni	150–200	1	tetralin
Benzene + $3H_2$	Ni	150–160	1	cyclohexane
Phenol + $3H_2$	Ni		1	cyclohexanol
Benzene + $4\frac{1}{2}O_2$	V_2O_5	400–440	1	maleic acid
Naphthalene + $4\frac{1}{2}O_2$	V_2O_5	350–400	1	phthalic anhydride
Toluene + $1\frac{1}{2}O_2$	MoO_3; UO_2	400	1	benzoic acid
Anthracene + $1\frac{1}{2}O_2$	V_2O_5	400	1	anthraquinone

TABLE 106.—*Synthetic organic chemicals, including intermediates and finished goods, dyes, plastics, rubbers, medicinals, and others.**

	Production 1946 (pounds)	Production 1947 (pounds)
Cyclic	5,085,303,000	5,083,893,000
Acyclic	9,151,190,000	10,938,778,000

* Tariff Commission.

OTHER PATENTS

U. S. Patent 1,598,560, on the absorption of ethylene in sulfuric acid, then with water to form ethyl alcohol; 1,599,119, ethylene and sulfuric acid to make neutral ethyl sulfate; 1,574,796, on ethyl sulfuric acid and ethyl sulfate from ethylene and sulfuric acid, catalyzed by ferrous or cuprous salts; 1,460,545, production of ethylene from ethane in natural gas; 1,402,336, production of ethylene from ethyl alcohol; 1,779,710, ethylene glycol ester of abietic acid; 1,569,775, on the absence of exposed iron in methanol synthesis, and a chromium oxide-manganese oxide catalyst; 1,738,989, on methanol synthesis; 1,824,896, on formaldehyde formation followed at once by hydrogenation with the aid of a second catalyst; 1,861,841, on dehydrating aqueous acetic acid with carbon tetrachloride; 1,875,273, production of methyl alcohol by passing gaseous mixture of hydrogen and carbon monoxide in contact with a hot catalyst mass comprising 50 per cent by weight of reduced copper, 300° to 400° C. and 5 to 300 atmospheres pressure; 1,961,736-7, forming acetic acid from methanol and carbon monoxide, J. C. Carlin and N. W. Krase; 2,031,475, oxidizing catalysts, to J. C. W. Frazer; 2,040,233, preparing contact catalysts; 1,925,602, on a stabilized solvent for metal degreasing; and 1,907,875, on an apparatus for that purpose. Brit. Pat. 587,584, silver catalysts in the preparation of ethylene oxide from ethylene. U. S. Pat. 2,416,350. phthalic anhydride manufacture.

[45] *Ind. Eng. Chem.*, 20, 1330 (1928).

Problems

1. It is required to manufacture 1 ton of ethylene glycol. Assuming the yield to be 100 per cent, how much ethylene oxide by weight will be required, and how much ethylene in order to make the oxide required? Express the latter in weight, and in volume, as the number of cubic feet necessary. The weight of one cubic foot of ethylene is 0.0738 pound.

2. The formula for the heat of reaction for the formation of methanol in gas form from carbon monoxide and hydrgen is

$$\triangle H = -18{,}050 - 19.54T + .01586T^2.$$

It applies to any temperature; the heat value is found by substituting for T the temperature of reaction in absolute degrees (or degrees Kelvin).

This expression is derived from the free energy expression

$$\triangle F = -18{,}050 + 45.00T \,.\log_{10}T - .01586T^2 - 69.4T.$$

The change in free energy for a reaction is of more importance and influence than the heat effect.

The exact value for the heat of reaction in the table is $\triangle H_{298} = -24{,}059$ gram-calories or -24.059 Calories. Check this value, and find the heat effect for 400° C., 300° C., and 325° C. Compare the results. In every case, it is for how many grams of methanol?

3. The reaction for making methanol is $2H_2 + CO = CH_3OH$. In order to make 100 gallons of methanol 100 per cent pure, how much hydrogen by weight will be required; how much by volume at 0° C. and 1 atm.? The reaction is made to take place at 300° C. and 1000 atm., so that the gases entering the catalytic chamber are put under that pressure and raised to that temperature. What will be the volume of the entering gases which actually do react?

But the conversion is 25 per cent; what is the weight and volume of the gases sent into the converter?

The catalytic volume is 10 liters; with the outgoing methanol assumed to remain gaseous, and the 100 gallons to be obtained in a period of 10 hours, what is the space velocity?

Calculate the volume of the compressed gases in two ways, first, according to the gas laws; second, with the use of the compressibility coefficients:

Temp. ° C.	Pressure Atm.	Hydrogen	Carbon monoxide	Methanol
0	1	1	1	1
300	1000	2.8157	3.3203	3.3

(*Compare* problems in Chapter 6.)

4. Chlorhydrin, $OH.CH_2.CH_2.Cl$, reacts with ammonia, NH_3, to form three amines,

Monoethanolamine $(C_2H_4OH)NH_2$
Diethanolamine $(C_2H_4OH)_2NH$
Triethanolamine $(C_2H_4OH)_3N$

These in turn are capable of reacting with acids such as stearic acid, $C_{17}H_{35}COOH$, to form soaps which are excellent emulsifying agents.

(1) Assuming commercial triethanolamine to contain 17.5 per cent DEA. and 5.0 per cent MEA., what is the theoretical yield from 1000 lbs. of chlorhydrin?
(2) What is the combining weight of the commercial TEA.?
(3) What weight of NH_3 is required for making the TEA. in (2)?
(4) What weight of stearic acid will combine with the commercial TEA. formed?

Reading References

"Acetylene and Carbon Monoxide Chemistry," J. W. Copenhaver and M. H. Bigelow, New York, Reinhold Pub. Corp., 1949.

"Production of ethylene from ethane, propane," R. C. Schutt, *Chem. Eng. Progress*, 43, 103 (1947).

"Ethylene recovery, commercial hypersorption operation," Howard Kehde, R. G. Fairfield, J. C. Frank and L. W. Zahnstecher, *Chem. Eng. Progress*, 44, 575 (1948).

"Ethylene purification by absorption process," Ludwig Kniel and W. H. Slager, *Chem. Eng. Progress*, 43, 335 (1947).

"Hypersorption process for separation of light gases," Clyde Berg, *Tr. Am. Inst. Chem. Eng.*, 42, 665 (1946).

"Ethylene oxide as an intermediate," M. A. Phillips, *Ind. Chemist*, 22, 387 (1947).

"Significance of German acetylene developments," C. C. Monrad, *Chem. Met. Eng.*, 53, 120 (1946).

"Reppe's acetylene chemistry," M. H. Bigelow, *Chem. Eng. News*, 25, 1038 (1947).

"Phthalic anhydride manufacture from orthoxylene," I. E. Levine, *Chem. Eng. Progress*, 43, 168 (1947).

"Hydrogenation in practice and theory and the manufacture of hydrogen," E. F. Armstrong, *Tran. Inst. Chem. Eng. (London)*, 9, 139-157 (1931).

"Chlorinated solvents in dry-cleaning," D. H. Killeffer, *Rayon Textile Monthly*, 18, 31 (1937).

"Katalyse vom Standpunkt der chemischen Kinetik," Georg-Maria Schwab, München, Julius Springer, 1931.

"Canada's most important synthetic organic chemical industry," A. F. G. Cadenhead, *Chem. Met. Eng.*, 40, 185 (1933).

"Synthetic organic chemistry in industry," G. O. Curme, Jr., *Ind. Eng. Chem.*, 25, 582 (1933).

"Synthesis of benzaldehyde from benzene and carbon monoxide under pressure," J. H. Holloway and N. W. Krase, *Ind. Eng. Chem.*, 25, 497 (1933).

"Methanol from hydrogen and carbon monoxide," R. L. Brown and A. E. Galloway, *Ind. Eng. Chem.*, 20, 960 (1928); 21, 310 (1929); 22, 175 (1930).

"Reactions that occur on a methanol catalyst," D. F. Smith and L. L. Hirst, *Ind. Eng. Chem.*, 22, 1037 (1930).

"Higher alcohols formed from carbon monoxide and hydrogen," G. D. Graves, *Ind. Eng. Chem.*, 23, 1381 (1931).

"Catalyst for formation of alcohols from carbon monoxide and hydrogen, VII—Studies of reduction of methanol catalyst," R. Nussbaum, Jr., and P. K. Frolich, *Ind. Eng. Chem.*, 23, 1387 (1931).

"Catalysts for the formation of alcohols from carbon monoxide and hydrogen, II—Synthesis of methanol with catalysts composed of copper and zinc," P. K. Frolich, *Ind. Eng. Chem.*, 20, 1326 (1928).

"Mechanical features of synthesis at high pressures," Robert V. Kleinschmidt, *Trans. Am. Inst. Chem. Eng.*, 29, 21 (1933).

"A chart of products derived from acetylene," Alexander Lowy, *News. Ed., Ind. Eng. Chem.*, 11, 156 (1933); twenty commercially useful products are included.

"The catalytic action of surfaces," J. E. Nyrop, translated from the Danish, London, Williams and Norgate, Great Russell street, 1937.

"The mechanism of contact catalysis," Dr. R. H. Griffith, of the Gas, Light and Coke Co., Oxford University Press, London, 1936.

"Catalytic process in applied chemistry," T. P. Hilditch, New York, D. Van Nostrand Co., 1929.

"Some observations of ammonia and methanol catalysts," Alfred T. Larson, *Trans. Electrochemical Soc.*, 71, 345 (1937).

"Catalysts costs determine economy in contact processes," Hermann W. Mahr, *Chem. Met. Eng.*, 45, 313 (1938).

"Catalysis Inorganic and Organic," Berkman, Morrell, and Egloff, New York, Reinhold Publishing Corp., 1940.

"Catalyst manufacture: a growing industry," Earl C. Ray, *Chem. Eng.* (May, 1948).

"The acetylene chemical industry in America," C. J. Herrly, *Chem. Eng. News*, 27, 2062 (1949).

"Bauxite: dehydrogenation catalyst for styrene production," W. H. Wood and R. G. Capell, *Ind. Eng. Chem.*, 37, 1148 (1945).

"Catalysts in petroleum refining," Felix Heinemann, *Petr. Ref.*, 27, 273 (1948).

"Production and performance of ammonia-synthesis catalyst," G. L. Bridger, G. R. Pole, A. W. Beinlich, Jr., and H. L. Thompson, *Chem. Eng. Prog.*, 43, 291 (1947).

"Development, production, and performance of water-gas conversion catalyst," G. L. Bridger, D. C. Gernes, and H. L. Thompson, *Chem. Eng. Prog.*, 44, 363 (1948).

"Review of development of processes for synthesis of liquid fuels by hydrogenation of carbon monoxide," H. H. Storch, *Chem. Eng. Prog.*, 44, 469 (1948).

Through his activity in synthesizing dyestuffs, the chemist has become interested in dye application: the science of using the proper dye, whether artificial or natural, for a given fiber.

Chapter 26

Dye Application

In the application of dyes, two main factors must be observed: the character of the fiber, and the properties of the dyestuff.

The character of the fiber: Cotton consists of pure cellulose: it has very weak properties, either acid or basic. Silk and wool, in contrast to cotton, have pronounced acid and basic properties. Consequently dyestuffs with pronounced acid or basic properties can be applied directly to wool and silk; to cotton only special classes of dyes, among others the benzidine group, are direct dyes, and are used in the form of the sodium salt. In addition, coloring matter may be fastened to cotton in a roundabout way, by means of an intermediate compound called a mordant, or by building the dye in stages on the fiber.

The properties of the dyestuffs, whether acid or basic, soluble or insoluble, reducible or not, must be considered in their application; various classes of dyes require different methods.

The Character of the Fiber

Cotton. Cold concentrated sulfuric acid dissolves cotton. Warm dilute sulfuric acid forms hydrocellulose (hydrated cellulose) and the fibers swell; in the cold, diluted mineral acids have no action. Organic acids at room temperature have no action; at higher temperatures, the strength of the fiber is weakened. Diluted caustic, or milk of lime boiled with cotton without access of air, has no action.

Concentrated alkali causes the cotton filament to swell and the walls of the fiber to become cylindrical, resembling tiny glass rods. If the caustic treatment is performed while the cotton is under tension, so that the fiber cannot shrink lengthwise, the cotton develops a silk-like luster. This process is called mercerization. The affinity of the mercerized thread for dye is much greater than that of untreated cotton.

Silk. Cotton consists of a single substance, cellulose, whereas silk consists of two: the fibrous substance, fibroin, and the silk gum, sericin. The silk gum covers the fiber; it is soluble in alkali, but inasmuch as alkali cannot be used to remove it without injuring the fibroin, very concentrated soap solutions are used for this purpose. The silk threads of commerce are fibroin; and it is to this part of the original substance that the following remarks apply.

Concentrated mineral acids destroy silk; diluted acids are readily absorbed by silk; wool is acted on in the same way. Hot caustic soda will dissolve silk completely, but not so fast as wool.

Tin, aluminum, and iron salts are adsorbed by silk as well as by wool, with the formation of a metallic hydrate or an insoluble basic salt. The

treatment of silk with tin salts, especially the tetrachloride, has resulted in the development of a highly desirable silk fabric called *weighted silk*, which has properties similar to silk. The standard procedure usually consists in replacing with tin the weight loss incurred through degumming of the raw fiber, that is, about 25 to 30 per cent.

Affinity of silk for coloring matters is in general lower than that of wool; for instance, certain acid colors on silk are not as fast to washing as when applied to wool, but others are.

Wool. Virgin wool is of many qualities, depending mainly upon the breed of animal. The fibers may be separated into the long ones, the tops, and the short ones (the noils) in the operation called combing. Worsted is made from tops only, while woolens are made from whole new wool, reworked wool, and noils. Wool is obtained from sheep and lambs, but many mills use also other fibers such as mohair, camel, vicuna, alpaca, goat, and other hairs, besides cotton, rayon, nylon, and other synthetic fibers.

When wool is treated with dilute mineral acids, it usually undergoes a series of chemical changes by the hydrolysis of higher protein complexes into lower simpler ones; there results a notably superior affinity for acid dyes, in comparison with that of untreated wool. Thus, wool which has been treated with dilute sulfuric acid and then washed with boiling water several times until the water shows a neutral reaction may be dyed in a neutral bath with a dye which ordinarily is applied in an acid bath. There is also a marked alteration in the colloidal structure of the fiber, which becomes highly receptive both to acid and basic dyes.

Wool is readily attacked by alkali; the higher the temperature, the more effective the attack.

This fiber behaves toward dye in different ways according to its origin, so that it is essential to obtain the wool from the same source, or be ready to make preliminary dyeings; but in all cases its affinity for dye is greater than that of silk, as stated previously. It will be remembered, too, that both wool and silk have a far greater affinity for dye than has cotton. Wool has pronounced acid and basic properties; it may be considered an amino acid. It is classed as a protein substance, as already implied.

Aluminum sulfate, ferrous sulfate, chrome alum, and other salts with acid properties are readily adsorbed by wool; neutral salts are not adsorbed. The application of salts to wool is called *mordanting*; it is an operation performed on a very large scale. Mordants are applied by the various processes known as pre-chrome, meta-chrome, and after-chrome dyeing, producing dyes which are extremely fast to light.

Rayon. In this synthetic fiber, a distinction must be made between viscose silk, or rayon, and cuprammonium rayon, on the one hand, and acetate rayon, on the other. The first two are essentially cellulose, and behave like cotton; they may be dyed in the main by means of the cotton dyes. Acetate rayon is cellulose acetate, and has different properties; its affinity for dyes is distinct from the affinity cotton shows.

Cellulose acetate is considered to be a solid solution which has the property of dissolving certain dyestuff bases with great ease and uniformity.

Such dyestuff bases are usually of the water-insoluble type, and must therefore be applied in a highly dispersed state of subdivision in order to favor penetration.[1] Dye bases for cellulose acetate comprise certain amino-azo coloring matters and intermediates as well as amidated or hydroxylated (or both) ring compounds of the anthraquinone series. Certain amino bases may be applied in a first bath, then diazotized on the fiber and further developed in a second and third bath toward the final shade (for dark blues and deep blacks).

Acetate rayon is attacked by caustic soda, a hydroxyl group replacing the acetyl group. This may be turned to advantage by allowing only a slight attack and then applying dyestuffs which would not be received were the hydroxyl group absent.

Nylon. This distinctly new material, already described in Chapter 22, is in one of its varieties, a superpolymer (molecular weight above 10,000) of hexamethylene diamine and adipic acid. Made into a fiber, it was the first truly synthetic fiber, and has a closer similarity in both constitution and properties to natural silk than has any other. Nylon fiber has the appearance and luster of silk; the degree of luster can be modified as desired by the use of a delusterant. Its tensile strength is higher than that of wool, silk, rayon, or cotton. The best dyes for nylon are the so-called acetate colors, although by introducing modifications it may be possible to use silk dyes.

"Fiberglas." Glass fibers already briefly discussed in Chapter 11, are now being produced in a number of shades, including tans and browns. These fibers could not be dyed in the usual sense, but they need not be, for they are colored in the glass batch. Special methods are used to spin the fibers, but weaving is done in the usual manner. The glass fabric is fireproof and becomes of value for scenic drops, stage curtains, and tablecloths. Another use which depends upon the inertness of the fabric is in the form of filter cloth for the filtration of high concentration acids and alkalies, a plant application of the laboratory filter medium, glass wool. The fabric is also used for ladies hats and wearing apparel.[2]

The Properties of Dyestuffs

Dyestuffs are chemical compounds which have the property when in solution to color animal or vegetable fibers permanently, with or without the use of auxiliary agents. They may be divided into natural [3] and synthetic dyestuffs, with the latter class now the more important; but the color chemist divides all dyestuffs rather on the basis of whether or not preliminary or after-treatment is necessary in applying the dye to the fiber. From this point of view, dyestuffs may be divided into: Substantive dyestuffs (cotton); basic dyestuffs; acid and chrome dyestuff; diazotized developed dyes; sulfur

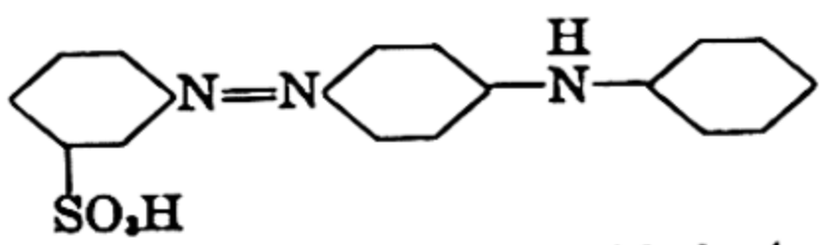
[1] *Chemical News,* 128, 19 (1924), also a number of articles in volumes 14 and 15, of the *American Dyestuff Reporter.*

[2] "Fiberglas, decorative yarns and fabrics," *American Dyestuff Reporter,* 30, No. 5, p. 115.

[3] Areas of cultivation and production figures for natural dyestuffs will be found on p. 54 of Putnam's *Economic Atlas,* London, George Philip and Son, Ltd., and New York, G. P. Putnam's Sons, 1925.

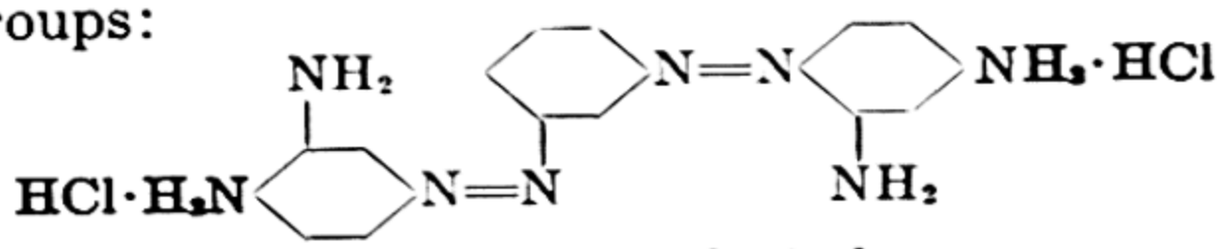
dyes; vat dyes, and others. Direct dyes for wool and silk might better be described as acid and chrome dyes, which have a direct affinity for these fibers, and it might be added that many direct dyes for cotton are also excellent dyes for wool and silk. This system of classification will be used in the following discussion, but first the meaning of the terms *acid dyes* and *basic dyes* will be made clear, because these expressions are in constant use.

Acid dyes are dyes which have a pronounced acid character; they are mainly sulfonic salts of azo bodies, or sulfonic derivatives of basic dyes; but acid dyes do not include the direct dyes for cotton, such as the benzidine class, even when these contain an acid group.



Metanil Yellow, an acid dye[4]

Basic dyes are hydrochlorides, sulfates or oxalates of organic bases; by the latter is meant a substance containing besides a benzene or other aromatic nucleus, an amino group or certain other groups containing nitrogen. Thus Bismarck Brown is the hydrochloride of a basic azo dye containing four amino groups:



Bismarck Brown, a basic dye

Other basic dyes are Malachite Green, which is a triphenylmethane dye, and Methylene Blue, a thiazine.

Direct Dyes for Cotton. Direct dyes for cotton are sodium salts derived from benzidine, primuline, and a few other bases which contain sulfonic (SO_3H) or carboxyl (COOH) groups; such sodium salts have direct affinity for cotton. They are applied in a neutral or slightly alkaline solution. Examples: Congo Red and Brilliant Yellow.

Direct Dyes for Wool and Silk. Acid dyes are direct dyes for wool and silk; they are manufactured and shipped to the textile mill in the form of the sodium salts of such dyes, but the dye bath is made acid by adding sulfuric or acetic acid, so that the free dye is formed, that is, so that the sulfonic or carboxyl groups are free; in that state the dye is readily adsorbed by the animal fiber.

The basic dyes are direct dyes for wool and silk, that is, they have the property of dyeing silk or wool without the use of a mordant, in contradistinction to cotton, where a tannin, tartar emetic or other mordant is essential for proper fixation.

Indirect Dyes. The basic dyes are indirect dyes for cotton, for the latter must first be treated with tannin; as tannin is the mordant, this use of basic dyes entitles them to a place among the mordant dyes. Among the latter, the tannin dyes are relatively unimportant.

[4] The hexagon stands for benzene, C_6H_6; when a group (thus $-SO_3H$) is attached to the ring, it is understood that the hydrogen at that place is missing.

Mordant Dyes. These comprise, in addition to the above, those dyes which require preliminary treatment of the cotton with a metallic salt solution, followed by immersion in an ammonia solution, before the dye is applied. The ammonia treatment precipitates insoluble metallic hydroxides on the fiber and in the fiber; to this hydroxide, the dye becomes fixed in its turn. These insoluble, stable, colored compounds of metal and dye are termed "lakes." Alizarine, originally a natural dyestuff, now made altogether synthetically, is an example; it gives different colors with different salts, red with aluminum or tin, red-brown with calcium, blue-black with iron, and purple with chromium salts. A total of over 200 dyes, derivatives of alizarine or closely allied to it, forms the class called alizarine dyes; the original alizarine, which is also the simplest, is still widely used; its formula is given in the next chapter.

Chrome Dyes. Chrome dyes may be applied on wool by three different methods (1) by premordanting; (2) aftermordanting and (3) by the metachrome process (simultaneous addition of dye and mordant). In aftermordanting, a direct dye is first applied to wool in an acid bath; the wool is then treated with a solution of sodium dichromate, resulting in the formation of a chrome lake on the fiber. There is a fourth method, much simpler than the foregoing, which applies to the use of premetallized dyes; they are dyed like direct dyes or acid dyes. One of the Diamond Blacks is a chrome black. Logwood Black is still used on silk in certain dye houses in preference to other blacks because of its exceedingly rich bloom and fullness.

Sulfur Dyes. Sulfur dyes are cotton dyes; they must be reduced with a solution of sodium sulfide (Na_2S), forming a soluble compound called leuco [5] compound, which is adsorbed by the cotton. The dye is then re-oxidized (called development) in the air, and the insoluble sulfur dye is thus re-formed on the fiber itself. Such a process of re-forming the insoluble dye from its soluble leuco compound makes it extremely fast. Examples: Sulfur Black, Sulfur Blue.

Vat Dyes. Vat dyes are primarily cotton dyes; and like sulfur dyes, are insoluble in water. They are reduced with sodium hydrosulfite [6] ($Na_2S_2O_4$), with formation of the leuco compound; the latter is soluble in alkali, forming color solutions ranging from colorless to every shade in the spectrum. The sodium salt of the leuco compound has a marked affinity for cellulose, often superior to that of a better direct dye. By exposing the treated cotton to the air, the original insoluble dyestuff reappears, fixed to the fiber so that it cannot be washed out. Examples are Indigo and Indanthrene; both are fast, Indanthrene extremely so. The formula of both these substances is given in Chapter 28.

Soluble Vat Colors. Of increasing importance are the indigosols—the sodium or potassium salts of the sulfuric acid esters of reduced vat dyes. These leuco sulfuric acid esters are extremely stable in neutral or alkaline

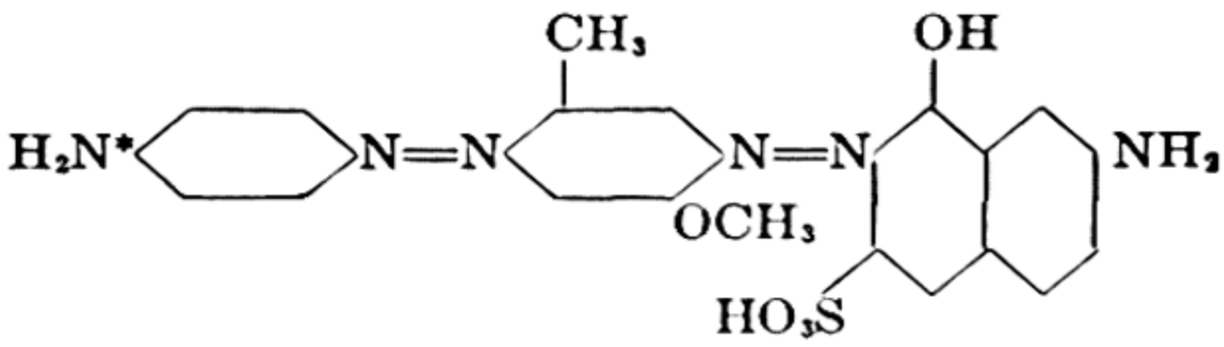
[5] The term leuco compound is applied solely to the soluble reduced body formed from the insoluble dye by reduction.

[6] The correct chemical name is sodium hyposulfite. It is erroneously called sodium hydrosulfite or hydrosulfite in the trade. In this chapter, the usage in the dyeing trade will be followed.

medium. When applied to the fiber (printing or dyeing) and subjected to an acid treatment in the presence of an oxidizing agent, *e.g.*, $NaNO_2$, they readily hydrolize, reverting to the original form of the vat dye. In fastness they are fully competitive with the vat dyes applied by the conventional caustic soda-hydrosulfite ($Na_2S_2O_4$) reduction method. They offer a certain ease in handling and may be applied to fibers of animal origin.

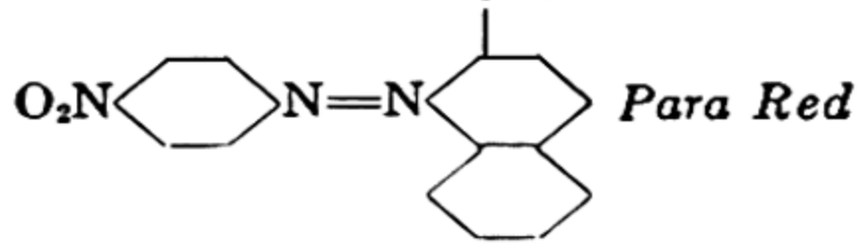
Developed Dyes. A distinction is made between "diazotized developed dyes" (which are soluble) and the so-called "ice colors" (which are insoluble), of which Para Red is a typical example. The diazotized and developed dyes are usually used to color plain grounds, which are later to be discharged (in part), with vat dyes for wash-fast, multi-color effects. Their fastness to washing is excellent by virtue of the extra diazotization and development method. The fastness to light is not necessarily better than that of the original dye.

The group of diazotized and developed dyes involves dyeing by means of a direct dye which has a free amino group, followed by diazotization on the fiber, and this in turn by coupling, so that another intermediate enters the molecule; it is a combination of direct dyeing and developed dyeing. For example, Zambesi Black D involves the following operations: The direct dye whose molecule has the composition



is applied to cotton as a direct dye; the color is black with a red tinge. The goods are now passed into a bath containing sodium nitrite and acid, where the amino group marked is diazotized. Next the goods are passed through a solution of β-naphthol, which couples on the new diazo group, forming a full, deep black. The reaction for diazotization and the one for coupling are given in the chapter on dyes.

An example of an insoluble and developed dye or "ice color," manufactured on the fiber is as follows. The cotton fiber is treated with β-naphthol dissolved in caustic soda, and is then passed through a diazotized paranitraniline solution; the formation of the dye takes place on the fiber.



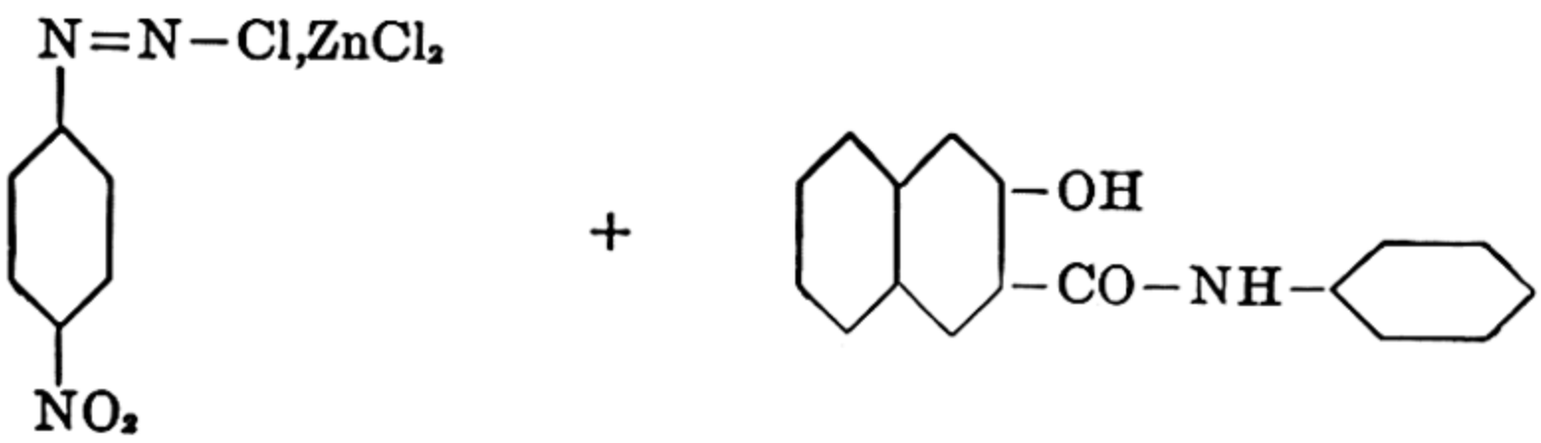
Para Red

A series of new "ice colors" is now produced by means of the Naphthol AS (1) coupling components and various forms of stabilized diazo compounds. The latter comprise the Fast Color Salts (2), the nitrosamine or Rapid Fast Colors (3), the Rapidogens (4) and the Rapidazols (5).

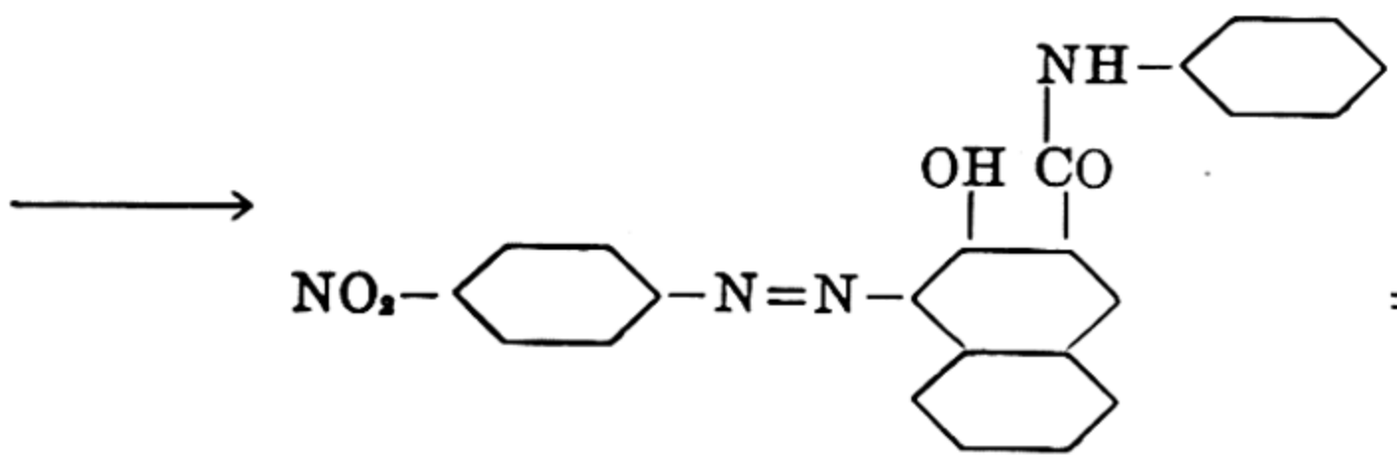
(1) The Naphthol AS coupling components are similar to β-naphthol, but possess a greater affinity for cellulosic fibers. They are derived from β-oxy-

naphthoic acid condensed with an amine such as aniline (Naphthol AS) to form a hydroxy naphthoic acid amide. Applied on the fiber in caustic solution and made to couple with an active diazonium chloride such as a Fast Color Salt, they produce highly brilliant color combinations, fast to light and washing.

(2) Fast Color Salts are stable diazotized aromatic amines usually obtained in the form of a complex zinc double salt. Para Red for example, can be produced by passing a fabric prepared with Naphthol AS, directly into a solution of the Fast Red Color salt without resorting to diazotization. Fast Color Salts are used in both dyeing and printing.

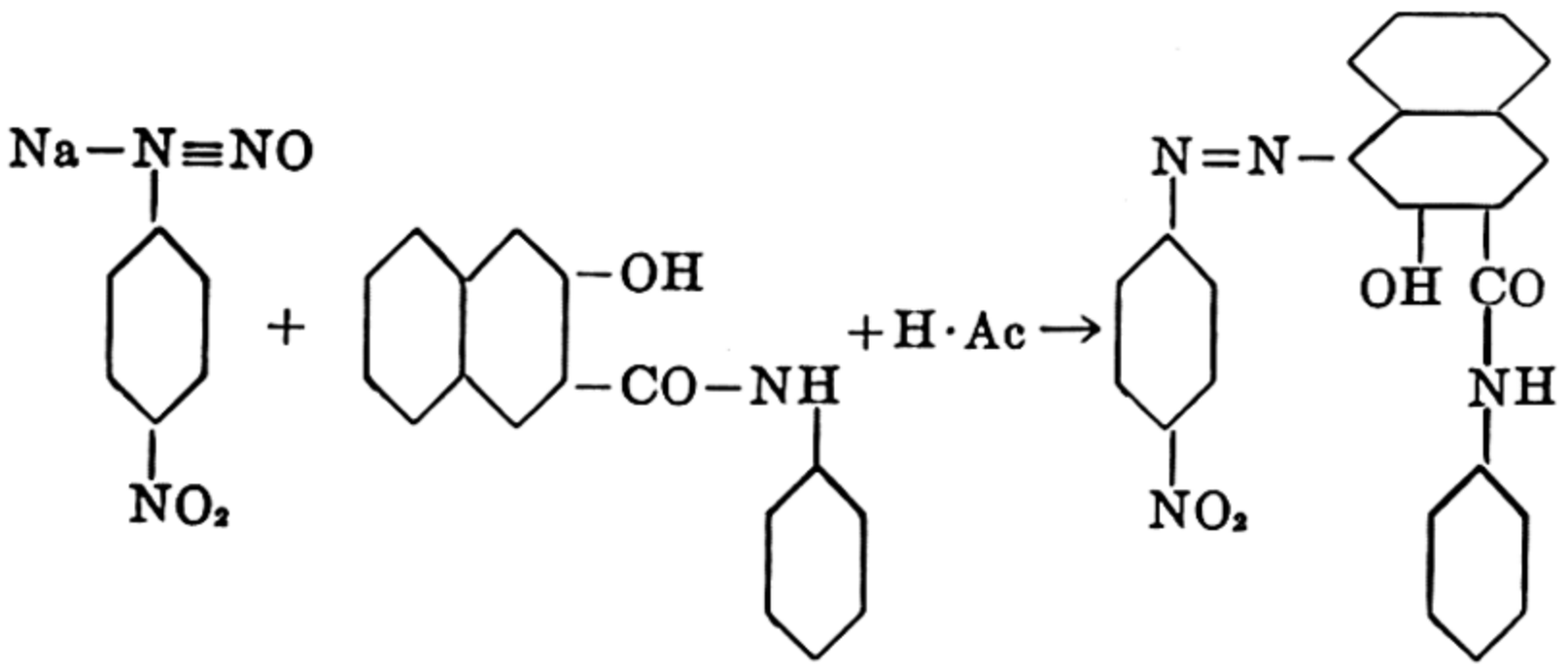


Fast Red Salt *Naphthol AS*



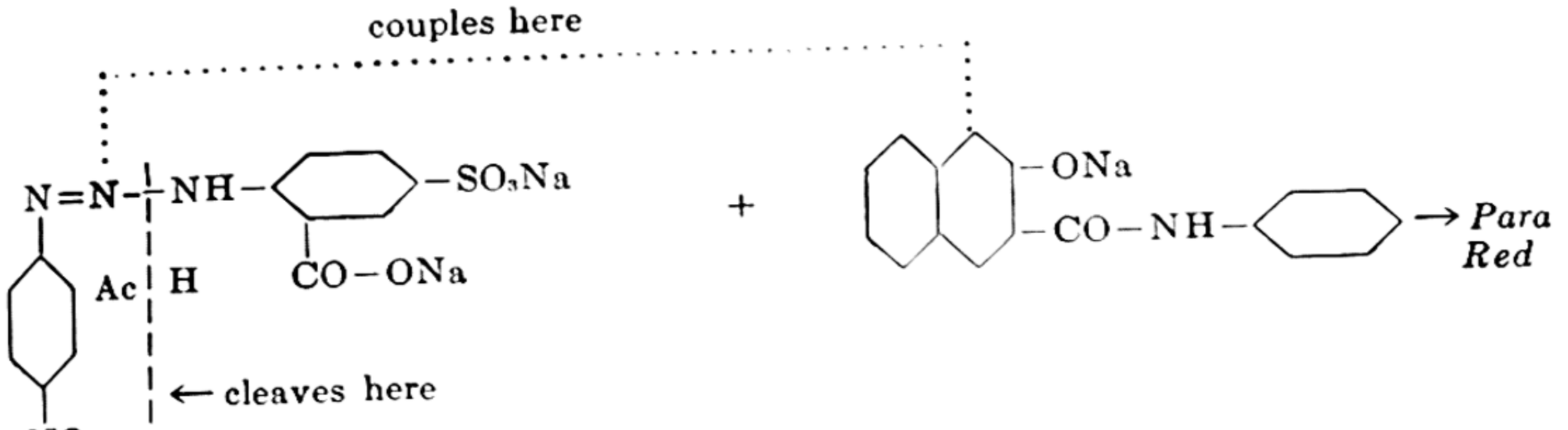
=*Para Red* of improved fastness

(3) The Rapid Fast Colors are mixtures of the nitrosamines of the diazo bodies, and molecular proportions of one of the Naphthol AS components. They are applied to the fiber by printing only. The color is developed by acid or by steam. Coupling takes place as shown below:



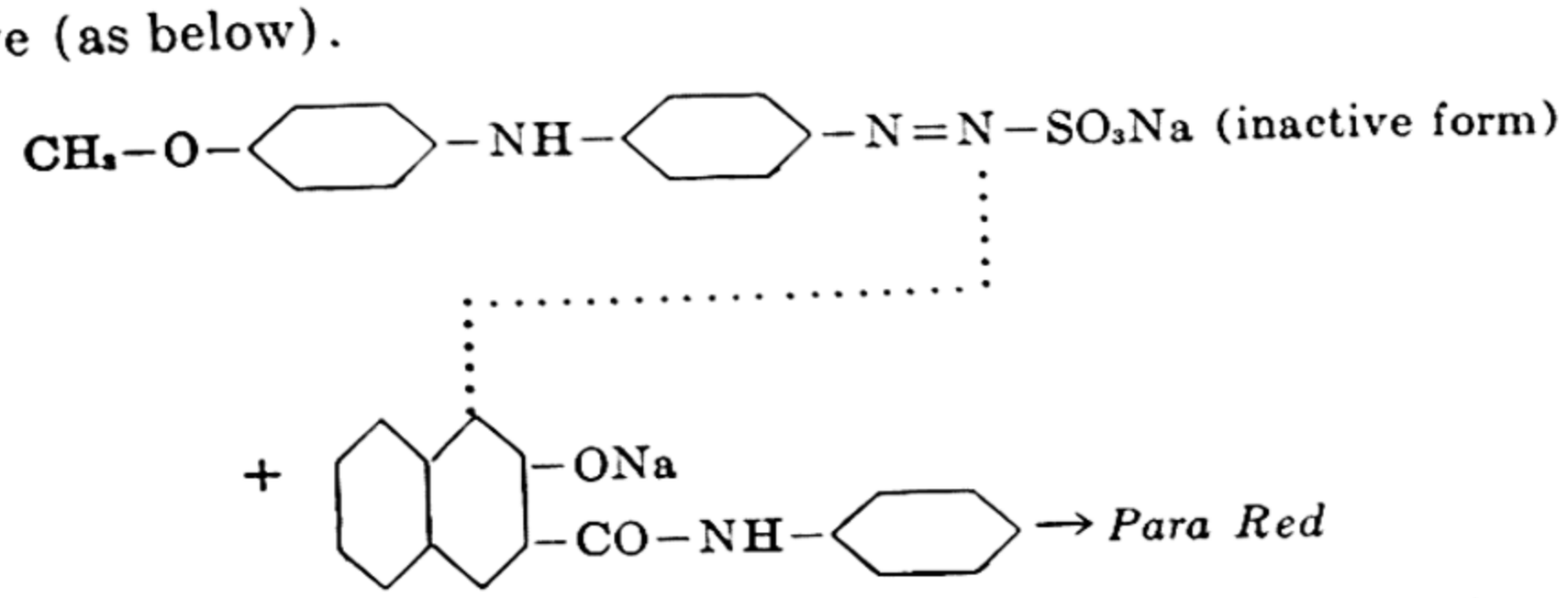
Naphthol AS *Para Red* of improved fastness

(4) The Rapidogens are compositions similar to the Rapid Fast Colors, except that the diazotate (Nitrosamine) is replaced by a soluble diazoamino compound stable in aqueous and alkaline solutions. The Rapidogen corresponding to the Para Red given above may be the following:



The color shades are developed in an acid medium by a passage through an acidified solution or in steam containing acidic vapors, such as those of acetic or formic acid. Until developed, there is no color. Rapidogens are compositions used exclusively for printing design on cotton and rayon materials, and to that effect are made into pastes with suitable thickening agents and applied to the cloth from engraved printing rolls; they yield extremely popular and brilliant color effects of excellent fastness to light and washing.

(5) The Rapidazols, much less important than either Rapidogens, or Rapid Fast colors comprise a restricted number of types limited to the production of dark navies and blacks. They are similar to the Rapidogens in composition, except that the diazoamino compound has been replaced by an aromatic diazosulfonate usually of a complex amino diphenylamine derivative (as below).



On prolonged steaming, the diazo sulfonate reverts to the active coupling form and produces the color, a dark navy blue in the example above, with the Naphthol AS.

Concentration of Dye on the Fiber. A light shade is obtained with 1 per cent dyestuff on the fiber, heavier shades by using 2, 3, 5, or even 8 per cent. In all cases the dye bath is worked until exhausted, frequently with the addition of Glauber salt which tends to render the dye less soluble. It must be especially noted that by 1 per cent is meant 1 per cent of the weight of the fiber; the percentage has nothing to do with the strength of the solution.

Mixing to Type. Dyes are usually manufactured in batches of 1000 pounds. No two batches are exactly alike. In order to obtain regularity of shade, a number of batches are mixed to give an average shade, which is called the type. Blending the various batches together is known as

"mixing to type." A difference between several batches would hardly be detected by the average person; to the trained eye it is evident.

Process of Direct Dyeing with Acid Dyes

Silk. Silk is placed in a bath containing the acid dye dissolved in the form of its sodium salt; enough dilute sulfuric or acetic acid is added to make the bath weakly acid. The dye bath is cold or lukewarm.

The dyes which may be used are, among many others: Ponceau, Crocein Scarlet, Eosine, Acid Fuchsine, Rhodamine, Rose-induline, Crocein Orange, Azoflavine, Methyl Yellow, Tartrazine, Patent Green, Alkali Blue, Patent Blue, Induline, Resorcin Brown, Naphthol Blue Black, Naphthol Black.

Wool. The dye bath is charged with the necessary amount of acid dye which dissolves, again in the form of a solution of the sodium salt; 2 to 4 per cent sulfuric or acetic acid is added in sufficient amount to liberate the free dye. The temperature is raised to 40°-50° C. and the wool introduced. Ten to 30 per cent Glauber salt, ($Na_2SO_4 \cdot 10H_2O$), based on the weight of the wool, is added and the bath slowly heated to boiling by direct steam. The dye leaves the bath and attaches itself to the fiber. If the dyestuff goes on too fast, the cloth is blotchy; this may be prevented by adding a levelling agent.

A slight modification of the method consists in dissolving the sodium salt of the dye for the bath, introducing the wool, and then adding the acid very slowly, in small portions.

The dyes which among others may be used for wool are the same as those listed under direct dyeing of silk with acid dyes.

Cotton. Before dyeing, cotton should preferably be boiled off with caustic soda or soda ash. A bleaching step should follow, especially in the case of light-shade dyeing. The cotton may then be introduced into the dye bath containing 2 to 5 pounds of dye for each 100 pounds of cotton, either as yarn in skeins, or as cloth; this is expressed as 2 to 5 per cent. One of the following salts is added to the dye bath: Glauber salt, common salt, borax, sodium phosphate, sodium carbonate. The bath is then brought to a boil and maintained there for some time, until the bath is exhausted of dye. The function of the salt added is to diminish the solubility of the dye, and thereby hasten the exhaustion of the bath. The cotton is next washed and dried.

The dyes that are suitable are members of the stilbene, benzidine, and primuline groups, such as Sun Yellow, Brilliant Yellow, Primuline Red, Congo Red, Direct Sky Blue, Direct Green B, Bordeaux, Scarlet and many others. Every shade is represented in these direct cotton dyes.

Many dyestuffs are precipitated by calcium and magnesium salts, so that a bath made up with ordinary ground water would result in precipitation of the dye; this is the reason why soft water must be used in the dye house.

Mordanting with Tannin

Mordanting with tannin concerns cotton chiefly. The cotton is placed in a hot water solution of tannin, and then in a lukewarm solution of tartar

emetic, for instance. Antimony tannate is now fastened to the fiber, and is insoluble. The goods are next passed slowly through a solution of a basic dye.

The basic dyes listed in the following division are suitable for cotton mordanted with tannin.

If the cotton is treated with sulfonated castor oil before mordanting, the dyeing is more even, and the fiber is more pliant (softer). This is true of every cotton dyeing. The concentration of the oil is 10 grams per liter or less.

Process of Direct Dyeing with Basic Dyes on Wool and Silk

For wool and silk, no tannin is needed, for they already contain an acid group in the molecule. The basic dye is dissolved in water, the temperature raised to 50° C., and the wool or silk is introduced. The temperature is raised further gradually, over a period of half an hour to the boiling point, when the process is completed. The material is washed with water and dried. Examples of basic dyes are: Fuchsine, Rhodamine, Safronine, Auramine, Phosphine, Malachite Green, Methylene Blue, Rosaniline, Mauve, Crystal Violet, Bismarck Brown. The first synthetic dye was a basic dye, Mauve.

Metallic Mordants

Wool and silk can dissociate certain metallic salts, so that when they are placed in the salt solution (such as aluminum sulfate), and boiled, the basic part of the dissociated salt deposits on the fiber. The rate of deposition is controlled by adding more or less potassium acid tartrate, which retards it. After that, the wool or silk is placed in the alizarine bath. Cotton mordanting with aluminum sulfate is no longer practiced. Vat dyes have displaced most alizarine and chrome mordant colors on cotton.

Examples of dyes applied with metallic mordants: Synthetic dyes—Alizarine, Alizarine Maroon, Purpurin, Anthrapurpurin, Anthracene Blue. Natural dyestuffs—Logwood, for blue and black, Cochineal, for red, Quercitron, for yellow.

In order to form lakes, hence to be adaptable to this kind of dyeing, the molecule of the dye must contain two hydroxyl groups in the ortho position to each other, or one hydroxyl group with one of the following groups in the ortho position: carboxyl, COOH, nitroso, NO, azo, N = N, and imide, NH.

Vat Dyes, Sulfur Dyes. The process for vat dyes and sulfur dyes is somewhat different, as these dyestuffs are first reduced in an alkaline vat with sodium hydrosulfite or sodium sulfide, respectively; the fabric is dyed in the reduced dye liquor (vat), then reoxidized by airing, by rinsing in cold water, or both. Sometimes a bichromate of soda-acetic acid treatment is given at this point. The fabric next is soaped and finished.

Apparatus

Wooden tubs have been used for acid baths, but acid-resistant alloys such as Monel and Allegheny metal are finding wide usage, because of the

ease with which traces of the dye can be removed when changing to another color. For neutral and alkaline baths, iron, steel and stainless steel are in common use. The dyeing may be done on skeins, or on the finished piece goods; in the latter case a device known as the jigger is used, shown in Figure 217.

Thread, wound loosely on a spool having a perforated winding surface, is dyed by pumping the dye solution through the windings from the center of the spool, and recirculating it until the bath is exhausted. This is known as the Franklin Process.

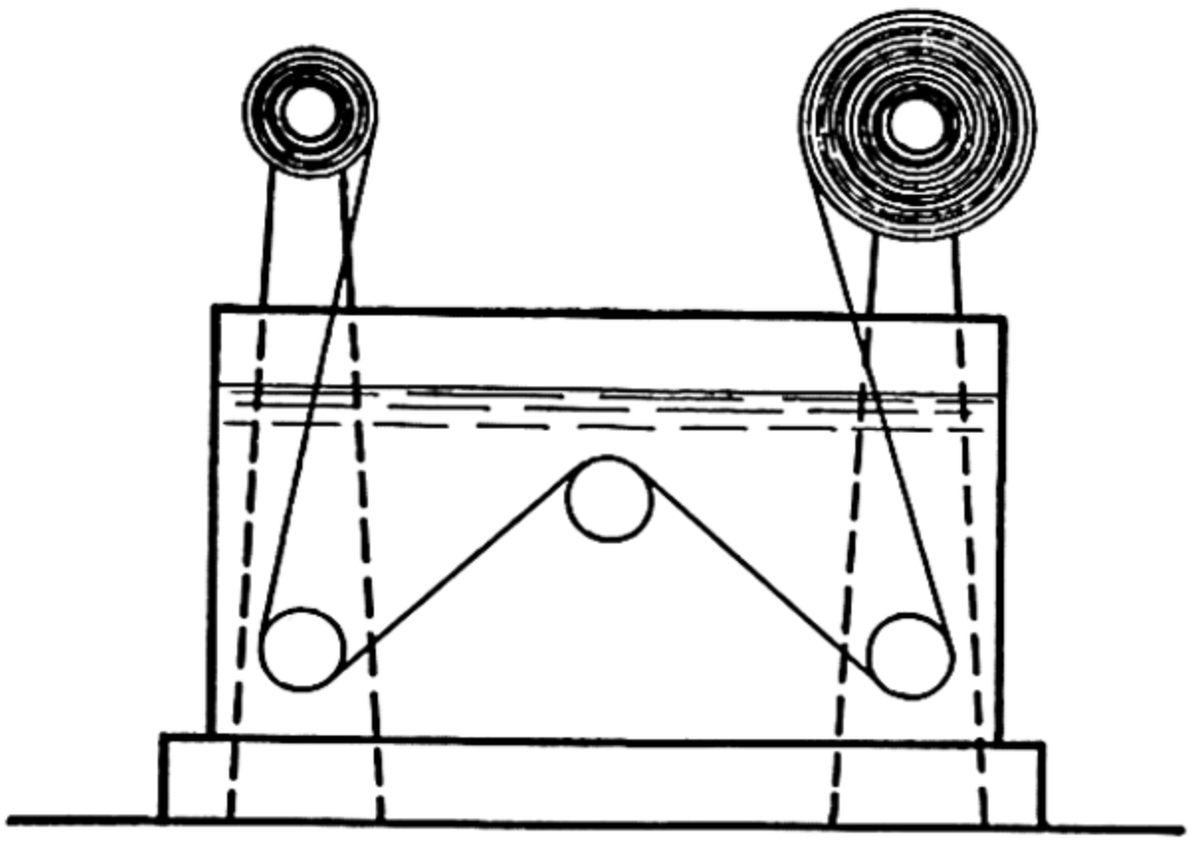


FIGURE 217.—The jigger, for dyeing piece goods. The goods are passed from one roll to the other through the bath, as shown, and then repassed in the other direction. There are generally six passes.

DESIGN FORMATION

Patterns in color may be produced on the piece goods by printing with copper rolls, using one of the three principles stated below.

1. In direct printing, the thickened dye solution is applied directly onto the desired spot on the white piece goods; the remainder of the surface remains as before. For instance, a polka-dot design may be printed in blue, from a copper roll having circular depressions filled with the dye solution. The blue dot on the white ground is formed directly. So that the color may not run at the edge of the dot, the solution is thickened by means of gelatin, starch, British gum or other material.

Example on cotton: A basic dye mixed with tannin, acetic acid, and a thickener, is printed on directly. The piece goods is steamed by passing it stretched over steam-heated hollow steel cylinders, and then washed. Usually a tartar emetic (antimonyl tartrate) treatment is given to improve fastness properties.

2. In reserve printing, certain uncolored substances are printed onto the cloth at the spots which should remain white. The whole is then dyed, and in the dye bath these substances repel the dye.

3. In the discharge method, the cloth is first dyed all over, and then there is printed onto it a substance which can destroy the dye by oxidation or reduction, leaving the spots reached by it uncolored. After the printing, the cloth is steamed, washed, and dried.

As discharge materials, stannous chloride, zinc dust and caustic, sodium bisulfite, sodium hydrosulfite ($Na_2S_2O_4$), and others may be used, thickened

properly by an inert material so that the applied discharge material will not run. Basic dyes are discharged by applying a paste of glucose, caustic, and a thickener; during the steaming, the reduction takes place.

Design formation by any one of these three methods is applicable to all fibers, with suitable modifications.

In Method 1 a mordant dye may be applied as well as a direct dye, as follows: The dye and the mordant mixed cold do not react appreciably; the two mixed with a thickener are applied. In the subsequent steaming, the dye and mordant react, and the produced lake is fastened to the fiber.

In general, the printing is done with copper rolls etched in the design needed. In the depressions, the printing paste is fed constantly from a trough, while the surface of the roll is wiped clean by means of a scraper, the "doctor blade." It is a form of intaglio printing. The printing may be very elaborate; as many as 15 rolls have been applied to the same piece of cotton or silk.

Wetting-out Agents. In order to dye evenly, it is essential that the dye solution should reach every spot on the fiber or cloth at the same time; this will occur only when the fibers are wetted at the same instant. The addition of certain substances favors even wetting with subsequent even dyeing, and these "wetting out" substances have assumed a major rôle. The most important wetting-out agents are soap, sulfonated castor oil, sulfonated naphthols, sulfonated abietene, and many members of the recently developed and already numerous synthetic detergents (over 125). Of first importance as wetting agents to the textile trade, synthetic detergents were developed in part as true detergents, replacing soap in hard water in which the synthetic detergent does not form curds, and replacing soap in acid solutions in which the latter is decomposed. A synthetic detergent may function as a detergent, a wetting, foaming, dispersing, emulsifying, or penetrating agent; it generally fills two or more of these functions. A closer examination of synthetic detergents will be found in Chapter 32.

Resin-treated Fibers. With the advent of modern plastics and resins, considerable use has been made of these materials to improve the tensile strength, resilience, durability, luster and firmness of fabrics. Some waterproof and weatherproof fabrics are attained by the application of a resin. The resin may be formed on the fiber or it may be applied directly, or by means of a solvent.[7]

A further development of the use of synthetic resins is pigment printing and dyeing. In these styles of color application the dye in the form of a pigment (lake, insoluble azo dye, vat dye, and others) is dispersed in a resin vehicle. The latter is thickened for printing purposes, and made fluid for dyeing purposes by the padding method. In either procedure, after printing or dyeing, the fabric is dried at high temperature to set the resin (curing), and finished. No washing is necessary. This mode of color application is extremely economical and produces surprisingly fast color effects.

[7] "Resins and Plastics for the Modification of Textile Fabrics," by D. H. Powers, *American Dyestuff Reporter*, 30, No. 3, p. 71.

Patents

U. S. Patent 1,865,701, manufacture of dyed rayon thread by precipitating the cellulose in filament form from a viscose solution impregnated with dyestuff in a reduced state and oxidizing the dyestuff to fix the color; 1,876,560, process of dyeing viscose rayon using tri-azo dyes, ($R_4 . N:N . R_1 . N:N . R_2 . N:N . R_3$); 2,023,387; 1,998,550; 2,015,500; 1,992,160; 2,000,559, wetting agent.

Conditioning fibers of organic derivatives of cellulose, U. S. Pat. 2,406,408; dyeing with indigoid vat dyestuffs, 2,420,729; apparatus and method for dyeing thermoplastic yarns or filaments, 2,405,669; dyeing casein fibers, 2,412,126-5; dyeing polyamide fibers (nylon), 2,421,151; dyeing nylon with gallocyanine dyes; acetate cellulose staple fiber treatment, 2,406,407-8, and 2,406,542; dyeing cellulose ester textiles with complex anthraquinone vat dyes, 2,242,857. U. S. Patents 1,954,702, leuco compounds of vat dyes; 2,145,193 vat dye compositions; 2,205,417, nitrosamine addition products; 2,122,424, diazo amino compounds; 2,067,926, vat dye compositions and manufacture thereof; 2,067,927-930, art of dyeing with vat dyes; 2,169,737, diazo amino compounds—methods of making and using same; 2,256,805-808, vat dye compositions and process of dyeing with vat dyes; 2,349,282, coloring of organic derivatives of cellulose; 2,270,756, coloring composition (use of Xanthinic bases) 2,407,704 and 2,430,771 anthraquinone acid dyestuffs and use on nylon, to Mr. Jean Kern.

Reading References

"Silk, a field for research," E. M. Shelton and T. B. Johnson, *Ind. Eng. Chem.*, 22, 387 (1930).

"Reaction of wool with strong sulfuric acid," Milton Harris, Ralph Mease and Henry Rutherford, *J. Res. National Bur. Standards,* 18, 351 (1937).

"Washing and fulling of woolen cloth preliminary to piece dyeing," Erich Wünderlich, *Dyestuffs,* 34, 215 (1936); translated from *Deutsche Färberzeitung.*

"Wool scouring," R. A. C. Scott, *Rayon Textile Monthly,* 18, 9, 98 (1937).

"The compression of wool by twist," James H. Fischer, *Rayon Textile Monthly,* 18, 251 (1937).

"The constitution and properties of cellulose," Harry LeB. Gray, *J. Chem. Ed.,* 7, (2), 1803 (1930).

"Nylon as a textile fiber," G. P. Hoff, *American Dyestuff Reporter,* 30, 4, p. 85.

"Textile fibers: chemical and physical aspects," Jerome Alexander, *Ind. Eng. Chem.,* 31, 630 (1939).

"Scouring fabrics woven of synthetic fibers," Thomas Ashley, *Dyestuffs,* 35, 11 (1937).

"The synthetic dyestuffs and the intermediate products from which they are derived," Appendix I, "The application of the colouring matter," J. C. Cain and J. F. Thorpe, London, Griffin and Co., 1933, p. 400.

"Men and women's shoe and leather colors for spring, 1937," *Dyestuffs,* 34, 209 (1936).

"Simple textile tests; tests to identify the most important textile fibers," *Dyestuffs,* 34, 194-200 and 205-208 (1936); translated from *Deutsche Färberzeitung.*

"The principles and practise of textile printing," E. Knecht and J. B. Fothergill, London, Chas. Griffin and Co., 1936.

"Reducing re-dyes on rayon crepes," Robert W. Pinault, *Rayon Textile Monthly,* 18, 257 (1937).

"Pocket guide to the application of the dyestuffs," Badische Anilin and Soda Fabrik, 128 Duane Street, New York.

"Resins and plastics for the modification of textile fabrics," D. H. Powers, *Ind. Eng. Chem.,* 32, 1543 (1940); and several other articles on new textile fibers, fabrics and finishes in the same issue, p. 1547-1573.

"National Nacconols" (an account of the properties, wetting ability, applicability of the Nacconols), *Dyestuffs,* 34, 67-82 (1935) (pub. National Aniline and Chemical Co., 40 Rector Street, New York).

"New wetting agents—sulfonated abietenes," I. Gubelmann, H. J. Weiland, and C. O. Henke, *Ind. Eng. Chem.,* 23, 1462 (1931).

"Wetting agents," F. E. Bartell, *Ind. Eng. Chem.,* 33, 737 (1941).

"Sulfosuccinic esters, structure and wetting powers," C. R. Caryl, *Ind. Eng. Chem.*, 33, 731 (1941).

"Surface-active agents, made in America, and commercially available," *Ind. Eng. Chem.*, 33, 16-22 (1941), a list of names, types, uses and manufacturers, compiled by F. J. Van Antwerpen, former Associate Editor.

"What's ahead for synthetic detergents?," *Chem. Industries*, 58, 964 (1946).

"The theory and practice of wool dyeing," C. L. Bird, Society of Dyers and Colourists, 32, 34 Picadilly, Bradford (England) 1947).

The intermediates are the link between the low-valued products of the distillation of coal tar and the valuable dyes. The manufacture of dye intermediates is the most brilliant success of synthetic organic chemistry.

Chapter 27

The Manufacture of Dye Intermediates

The group of synthetic compounds called intermediates is the starting point for the manufacture of dyes; they form the raw materials for the dye industry; to put it still another way, the intermediates are the foundations of the dye constructions. The name is certainly appropriate, for they are the intermediate compounds between benzene,[1] naphthalene, and anthracene, on the one hand, and the brilliant and varied dyes, on the other.

That benzene, naphthalene, and anthracene are obtained by distilling coal tar,[2] the evil-smelling black liquid found in the hydraulic main of an illuminating gas plant, and similar plants, has been stated in Chapter 14; to name the intermediates, "coal-tar intermediates," and the dyes made from them, "coal-tar dyes," as is often done, is therefore quite correct. In themselves, benzene, naphthalene, and anthracene are of little value; but by the introduction of SO_3H,NO_2,NH_2,OH, alkyl or other groups into the molecule, replacing a hydrogen atom, the body becomes important and valuable; it is then an intermediate. The number of known intermediates is enormous; the number of the possible ones, greater still.

The transformation of benzene, naphthalene, and anthracene into these substituted bodies is done by a variety of operations, the most important of which may be divided into the following classes:

1. Nitration, the substitution of one or more hydrogens by NO_2.
2. Reduction, for instance, of NO_2 to NH_2.
3. Sulfonation, the substitution of one or more hydrogens by the sulfonic group, SO_3H.
4. Halogenation, the substitution of one or more hydrogens by Cl, Br, or I.
5. Alkylation, the substitution of hydrogen by an alkyl group, such as methyl, CH_3, or ethyl, C_2H_5.
6. Alkaline fusion, the substitution of the sulfonic acid group, SO_3H, by the hydroxyl group, OH.

In the discussion of these operations it is important to distinguish between various isomers produced, that is, bodies alike in the groups they contain, but differing in the relative position of these groups, as for example the two nitrotoluenes shown below under Nitration. Such a distinction may seem a rather nice one, belonging to the scientific aspect of the subject, but it is in reality of the greatest practical importance, because the colors made later on by means of the separated isomers will differ. To obtain pure colors, an intermediate free from its isomers must be used

[1] Benzene is the same substance as benzol.

[2] The greater part of the benzene is obtained by "scrubbing" the gas from the distillation of coal, with oil, and recovering it from the oil by distillation.

It naturally follows that a firm producing impure intermediates, impure in the sense that a given body is still accompanied by its isomers, is likely to see its business dwindle.

It might be said further that two isomers often differ in a pronounced way in their properties, although the structural difference is very slight; for instance ortho-nitrotoluene is a liquid, but para-nitrotoluene is a white solid. The difference in properties is indeed sometimes slight, but there is always some difference in at least one property.

The compounds of carbon are exceedingly delicate; they react readily and always in several directions; for instance, while nitrating, some oxidation is almost unavoidable. This circumstance, added to the difficulty with isomer formation, renders the choice of processes and their supervision so difficult that only men well-trained in scientific organic chemistry can choose and supervise successfully. In no other branch of industrial chemistry does plant practice follow so closely the purely scientific treatment of the subject. Only the products of industrial importance and the well-established plant processes are considered in this chapter.

The apparatus is not simple; on the contrary, it is of many kinds, as would be expected at once when it is realized that there may be required a nitration, reduction, sulfonation, alkali fusion, halogenation, hydrolysis, with washings and purifications between stages. Thus the manufacture of some of the newer intermediates constitute a technology even more complex than that of the dyestuffs themselves. Wooden, cast-iron, steel and special steel vessels are used.

The system of notation in this chapter is the customary one: the hexagon means benzene, C_6H_6, unless otherwise indicated; the double hexagon means naphthalene, $C_{10}H_8$. When a substituting group is written in, the hydrogen atom is understood to have been removed to make room for the entering group.

Nitration

Ordinarily, nitration is performed in the cold, to render harmless the oxidizing tendency of nitric acid. The reaction for benzene is

$$\underset{\textit{benzene}}{C_6H_6} + HONO_2 \rightarrow \underset{\textit{nitrobenzene}}{C_6H_5NO_2} + H_2O$$

The water formed dilutes the nitric acid and rapidly inhibits its nitrating effect; in order to overcome this interference, commercial nitrations are performed with mixed acid,[3] such as

30 per cent nitric acid
60 per cent sulfuric acid
10 per cent water.

The sulfuric acid does not take part in the reaction, but serves as a diluent and an absorbent for the water formed during the reaction, thus maintaining the strength of the nitric acid.

Not only are hydrocarbons such as benzene nitrated, but very frequently substances in which there already are present other substituting groups. If the group NH_2 is present, it must be "protected" during the nitration, even

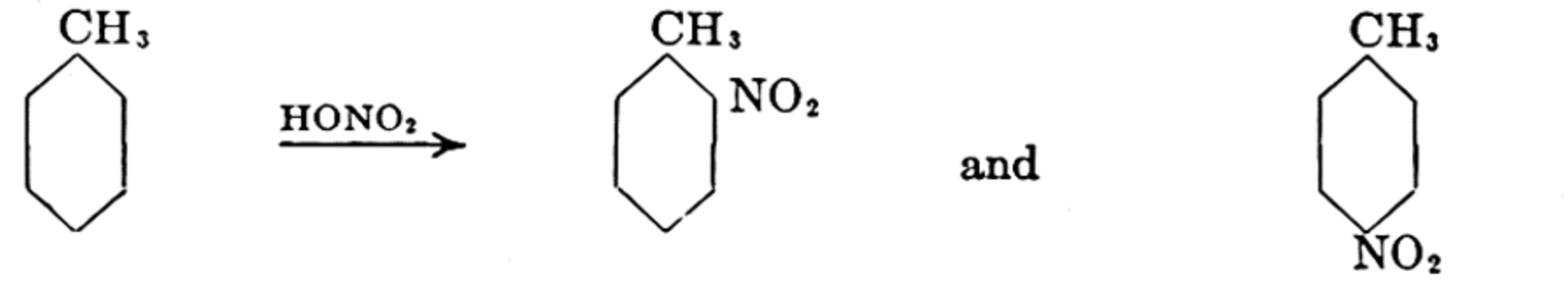
[3] Chapter 2.

though the temperature is low, to prevent its oxidation and consequent loss. This "protecting" is done by such means as acetylation, and the protecting group is removed after the nitration.

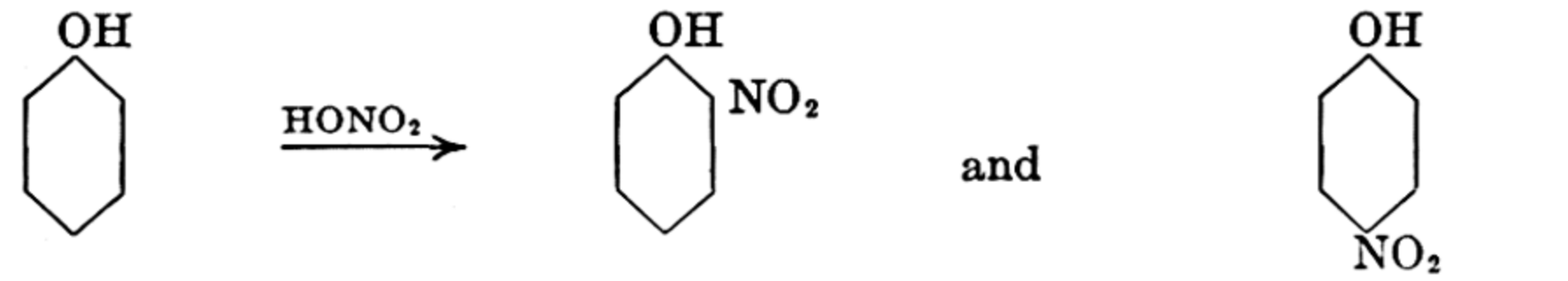
The groups already substituted in the molecule influence the position which the entering group takes, according to the following rule, given in two parts, with examples:

a. If any one of the groups CH_3, CH_2Cl, Br, I, OH, NH_2, and certain others is present, the nitro group enters mainly in the ortho and para position, sometimes only in the para position.

Examples:

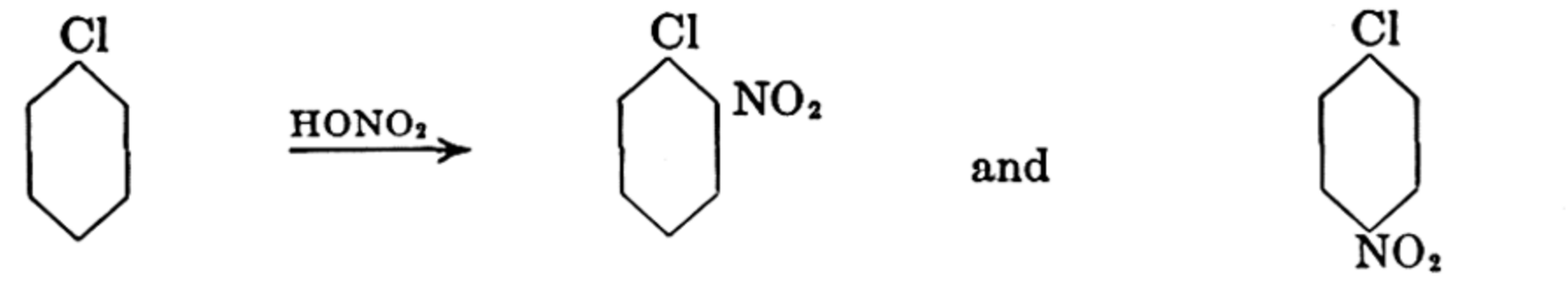


toluene (liquid) — *ortho-nitrotoluene* (liquid) and *para-nitrotoluene* (white solid)



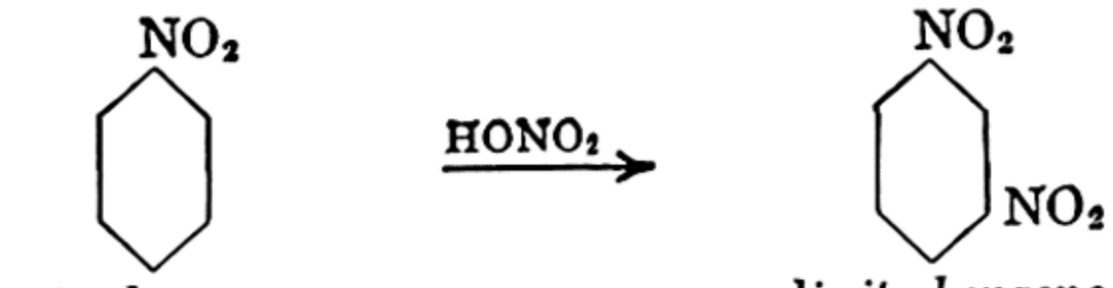
phenol (solid) — *ortho-nitrophenol* (yellow solid) and *para-nitrophenol* (white solid)

Ortho-nitrophenol and para-nitrophenol are isomers; they are separated by steam distillation, for the ortho body is volatile in the steam, while the para body is not, and therefore remains behind in the distilling vessel.



chlorobenzene (liquid) — *ortho-nitrochlorobenzene* (low-melting solid) and *para-nitrochlorobenzene* (solid)

b. If there is present in the molecule any one of the following groups: NO_2, COOH, CHO (the aldehyde group), or SO_3H, the nitro group enters mainly meta. Example:



nitrobenzene (liquid) — *dinitrobenzene* (solid)

When nitrating benzene to nitrobenzene, an excess of nitric acid must be avoided, otherwise dinitrobenzene is formed. The procedure is to run the mixed acid into the benzene, not the converse; this is a general rule, if a single substituting group is desired. About 2500 pounds of benzene are nitrated in one batch, and the time is 3 to 4 hours. Heat is evolved during

the reaction and is removed as fast as generated by means of cooling pipes laid in the benzene, or by means of cold water (or brine) circulated in the jacket surrounding the vessel; toward the end of the reaction, warm water is circulated in the jacket. (*See* Fig. 218.) Cast iron is used, since mixed

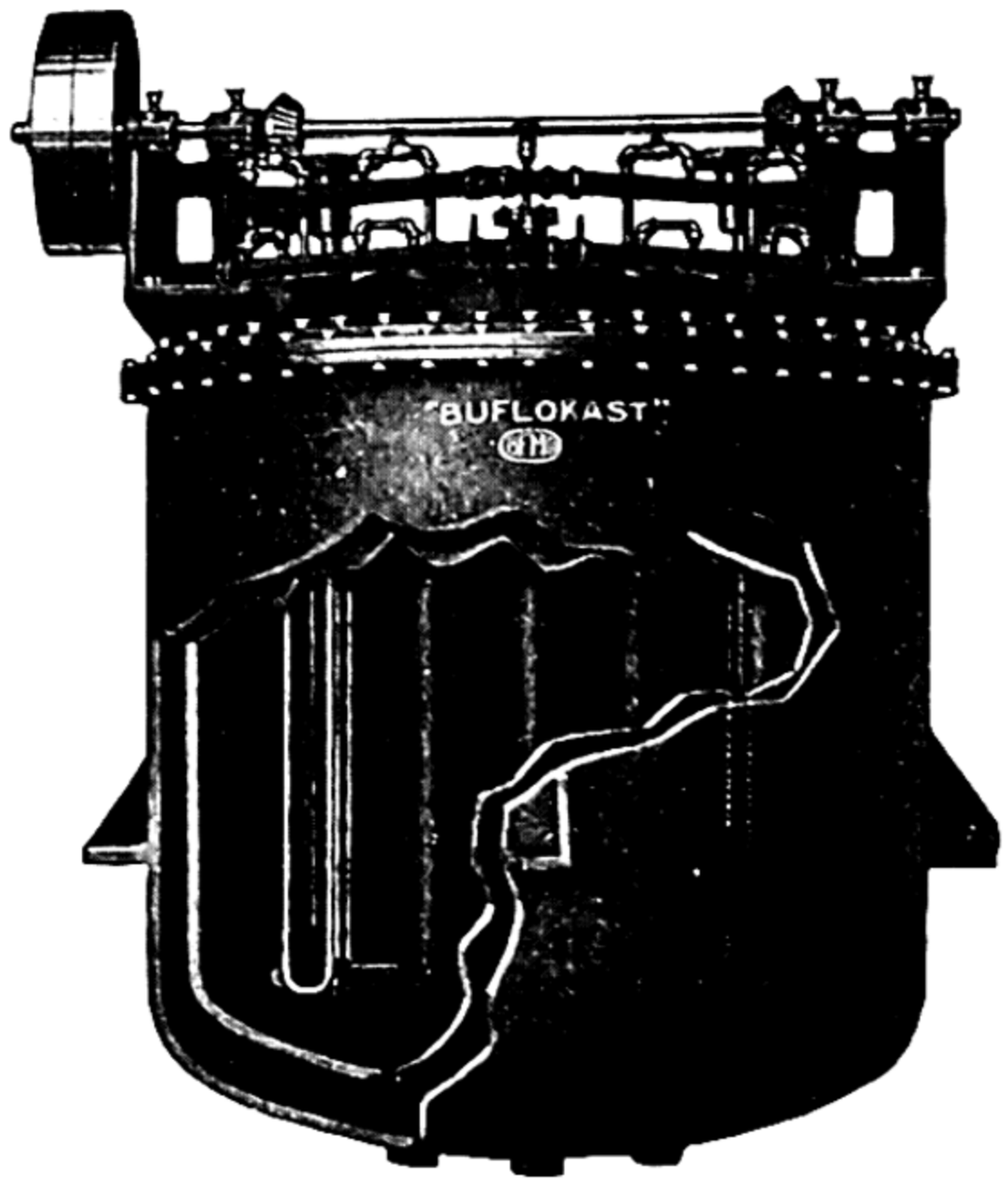
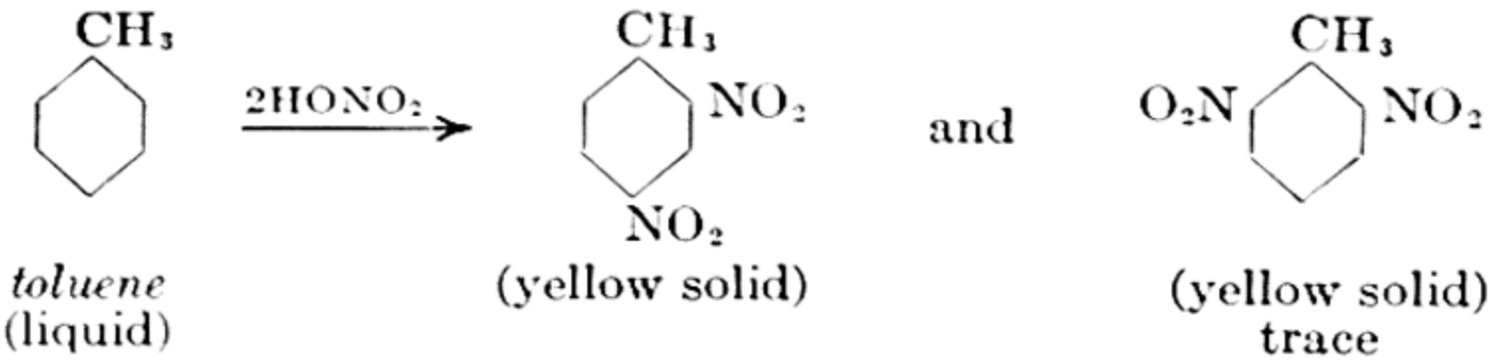


FIGURE 218.—Jacketed cast-iron nitrator, showing two impellers for agitation, and five cooling cells. (Courtesy of Buflovak Equipment Division, Blaw-Knox, Pittsburgh, Pa.)

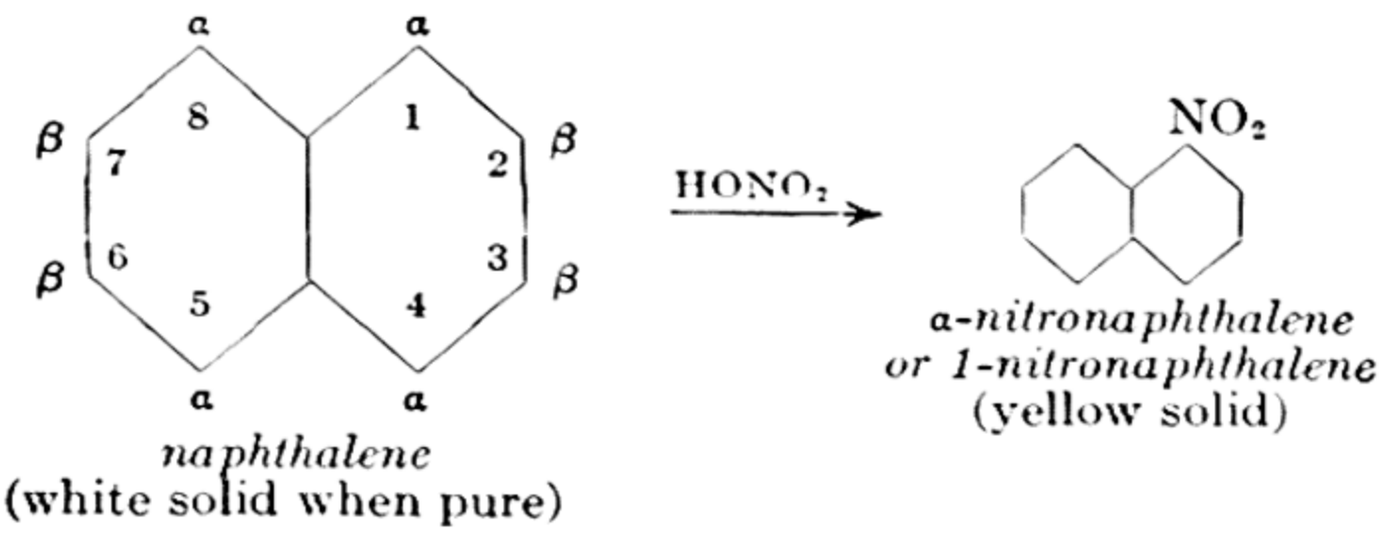
acid does not attack it. A stirrer is provided, for otherwise the benzene and the acid remain two separate layers. After the action is complete, the nitrobenzene separates out as an oil over the acid, and is removed by decantation. It is agitated with water or dilute alkali to remove small amounts of acid, and may then be distilled if pure nitrobenzene is desired.

When nitrated with enough acid to form two nitro groups, toluene gives two different dinitrotoluenes; the temperature is kept at 35° C.:



toluene (liquid) — (yellow solid) — (yellow solid) trace

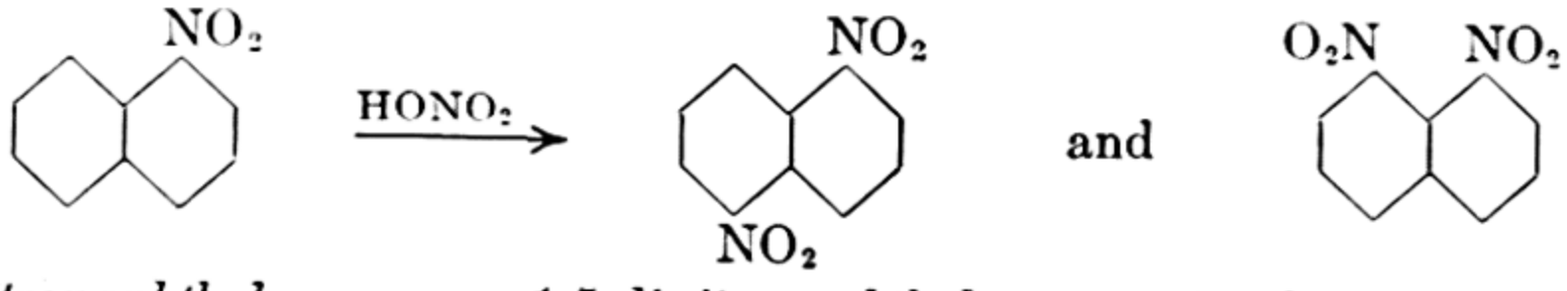
Naphthalene treated with the proper amount of mixed acid to form one nitro group gives mainly α-nitro-, and small amounts of β-nitronaphthalene:



naphthalene (white solid when pure)

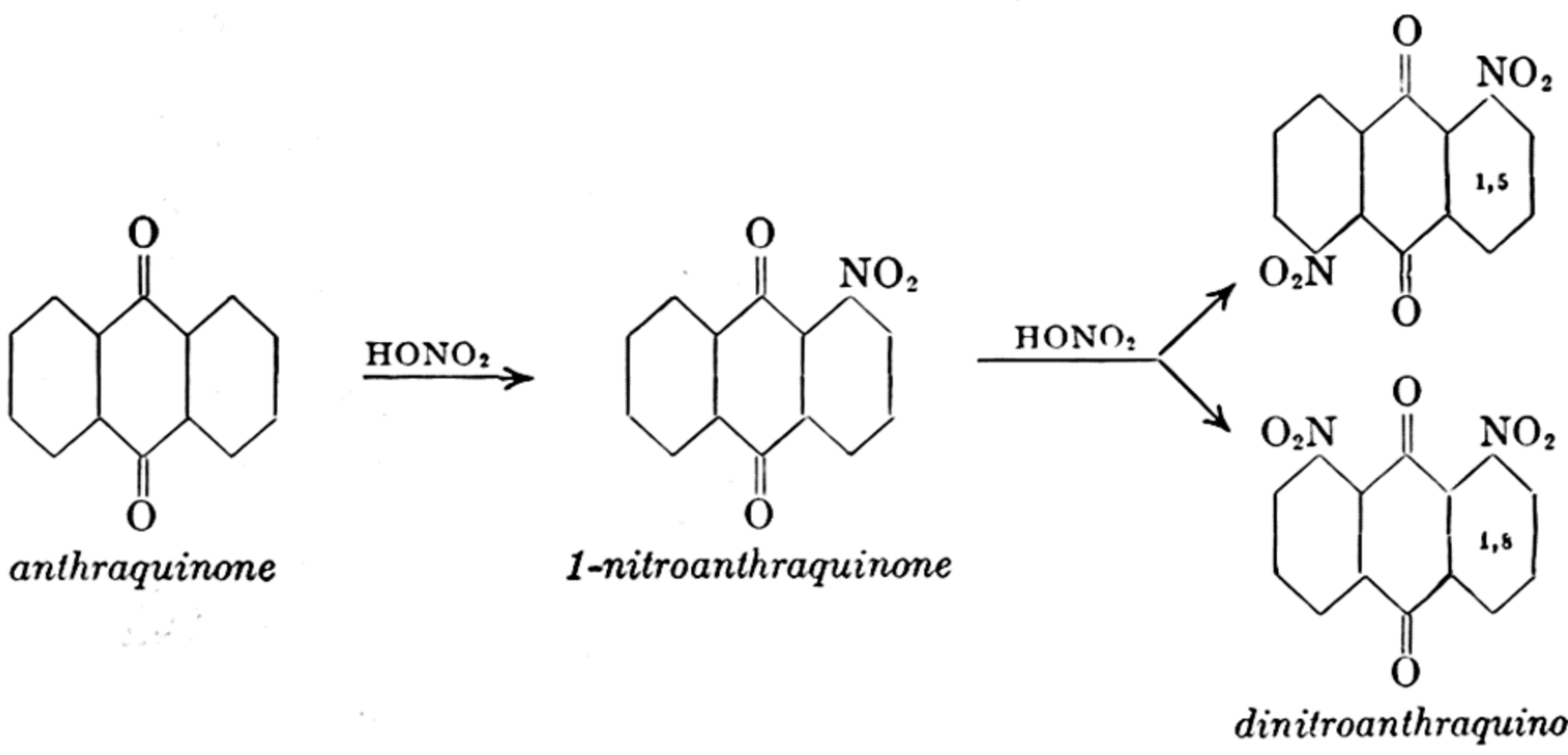
α-nitronaphthalene or 1-nitronaphthalene (yellow solid)

On further nitration, the mono-nitro body gives 1,5 or 1,8 dinitronaphthalene; the temperature is 70° C.; all three bodies are solids.



1-nitronaphthalene *1,5 dinitronaphthalene* *1,8 dinitronaphthalene*

Anthraquinone nitrated for one nitro group gives only α-nitroanthraquinone at 50° C.; a second group enters again α, producing the isomers 1,5 and 1,8 dinitroanthraquinone at 80° C.; all are yellow solids.



anthraquinone *1-nitroanthraquinone* *dinitroanthraquinone*

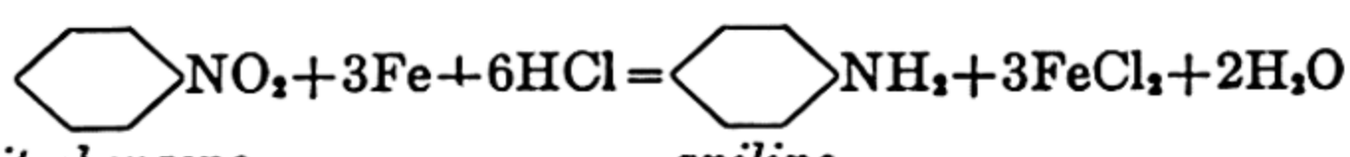
Hence, according to the amount of acid used, mono-, di-, or even trinitroanthraquinone compounds may be formed.

These nitrations are performed in cast-iron or steel vessels with steel agitators; a liquid requires no pre-treatment; a solid is dissolved in concentrated sulfuric acid, and this solution then treated with the mixed acid.

Reduction

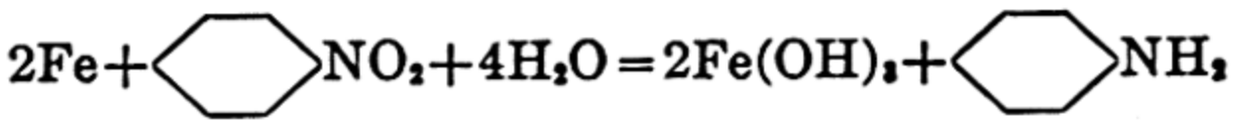
Among reductions, that of the nitro group, NO_2, to the amino group, NH_2, is a frequent and important one; several reducing agents may be used:

a. Iron turnings or powder and hydrochloric acid are generally used; less frequently tin or zinc with hydrochloric acid. The theoretical reaction is



nitrobenzene (liquid) *aniline* (liquid)

But in practice, one-fortieth of the amount of acid required by this reaction is sufficient, because the ferrous chloride formed catalyzes the reaction:



The nitrobenzene is placed in the reducer, a vertical cylindrical vessel provided with cover, steam jacket and a stirrer; the iron turnings [4] or powder

[4] Cast-iron turnings, crushed in a hammermill to pass through a 10-mesh screen, are to be preferred.

and the hydrochloric acid are added gradually, in small portions. A brisk reaction, but not violent, is maintained by means of steam circulated in the jacket, or blown into the charge directly. A condenser returns to the reducer any vapors which pass out. After the nitrobenzene is completely changed to aniline, a strong current of live steam is sent into the charge; a mixture of steam and aniline vapors passes out to the condenser and is collected in storage tanks. The bulk of the aniline separates as a lower

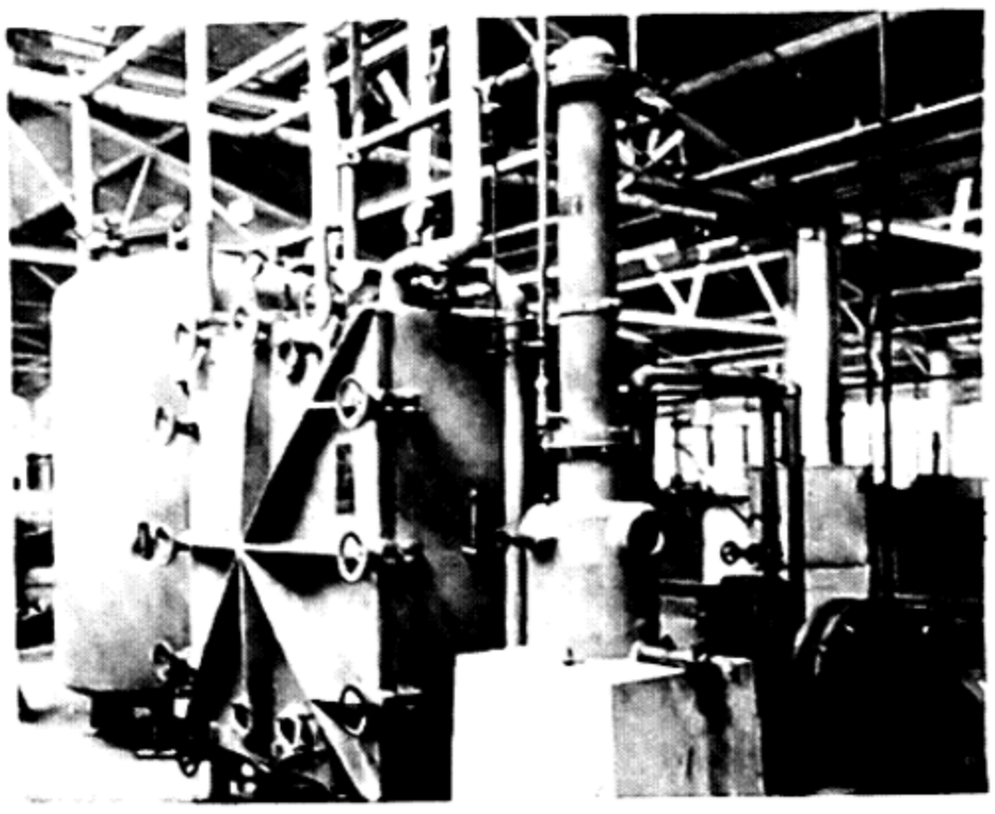


FIGURE 219.—A vacuum shelf drier, with condenser and vacuum pump. The shelves are hollow and receive steam. Such driers are used for intermediates and dyes. (Buflovak.) (Courtesy of the Buflovak Equipment Division, Blaw-Knox, Pittsburgh, Pa.)

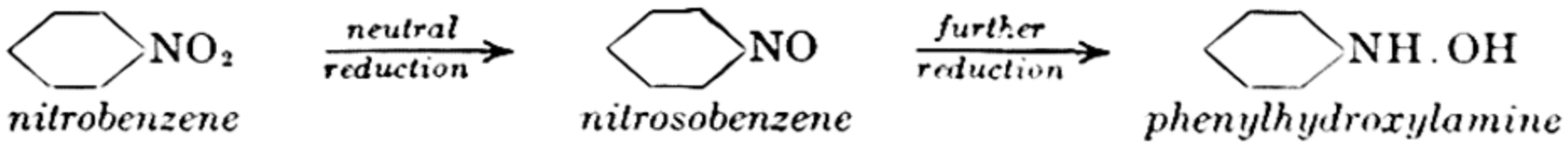
layer and is drawn off; the water over it still contains aniline, which must be recovered by distilling this "aniline water" again, or by extracting it with nitrobenzene. The iron hydroxide sludge is washed out of the reducer through a side outlet by flushing. A reducer 6 feet in diameter and 10 feet high takes a charge of 5000 pounds of nitrobenzene in one batch, and requires about 10 hours for the reduction. The aniline may be redistilled, when it is water white. There are many modifications of this method of reduction. The condenser consists of iron pipes laid in cold water.

Nitrobenzene may also be reduced to aniline, on a large scale, by means of hydrogen in the presence of Raney nickel.

Aniline is made from chlorbenzene, by treating the latter with ammonia in the presence of cuprous salts as catalysts. It is a continuous process, with ammonium chloride as a rather annoying by-product.[5]

Aniline hydrochloride is a widely used white solid, and is made by treating aniline with hydrochloric acid.

The reduction of nitrobenzene may be performed in acid, neutral, or alkaline solution and the products are in each case different. In acid solution, aniline is produced, as described above. In neutral solution, by means of zinc and ammonium chloride, phenylhydroxylamine results:

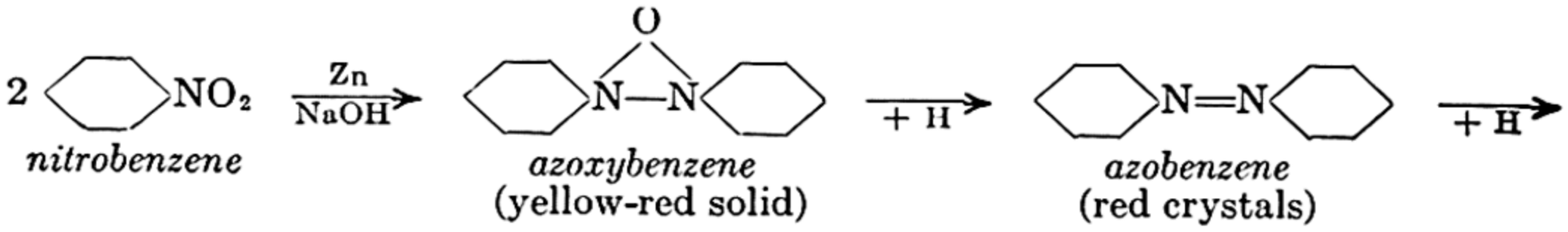


nitrobenzene *nitrosobenzene* *phenylhydroxylamine*

If the reaction is allowed to go too long, the phenylhydroxylamine is further reduced to aniline.

[5] U. S. Patents 1,726,170-3, reissue 17,280.

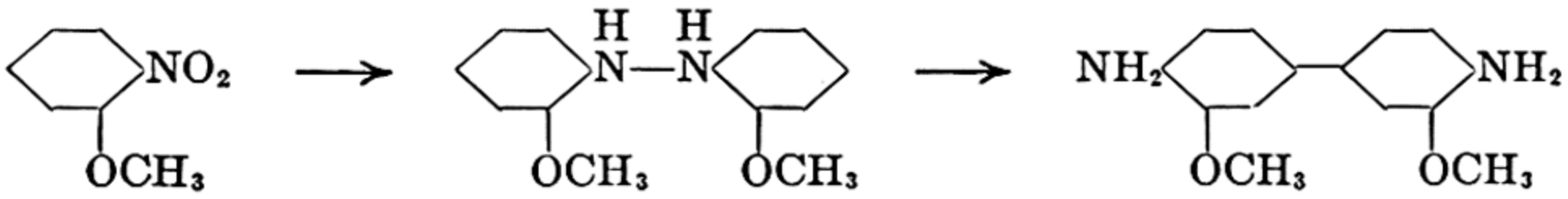
In alkaline solution azobenzene is formed, itself the starting point for benzidine:



nitrobenzene — *azoxybenzene* (yellow-red solid) — *azobenzene* (red crystals)

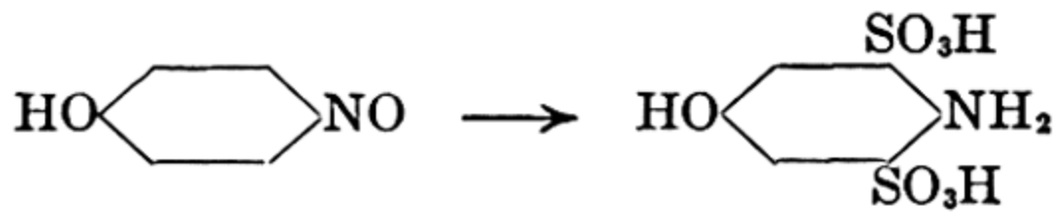
hydrazobenzene (white crystals) — *benzidine* (white crystals)

Alkaline reductions are performed, for instance, by means of zinc dust and caustic in water, or in hydrous alcohol; in addition to the example above, the following may be given:

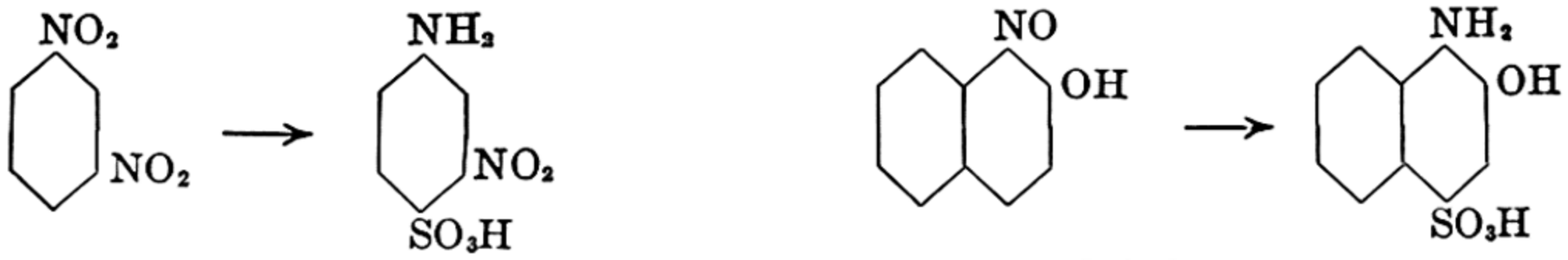


nitroanisole — *hydrazoanisole* — *dianisidine*

b. Sulfur dioxide as such, or its salt, sodium bisulfite, may be used for reducing, for instance, quinone to hydroquinone. When nitro or nitroso bodies are treated, the reduction is frequently accompanied by simultaneous introduction of the sulfonic group.

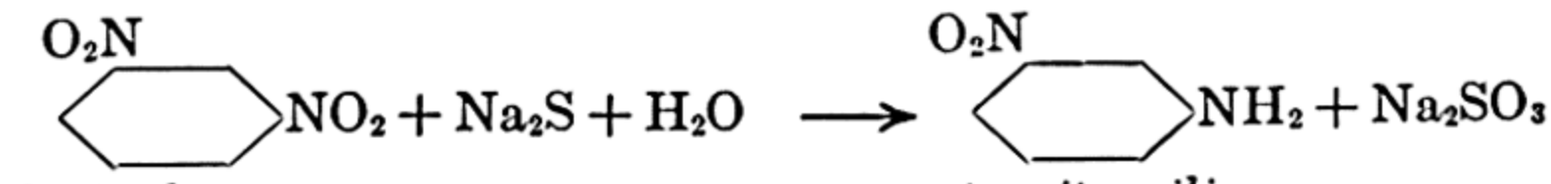


para-nitrosophenol



metadinitrobenzene — *nitrosonaphthol*

c. Sodium sulfide (Na_2S) is extremely valuable for reductions, as is also the disulfide, prepared by dissolving sulfur in a solution of sodium sulfide. For "partial reduction," that is, for the reduction of only one nitro group in a compound which has two, for instance, dinitrobenzene, sodium sulfide is usually chosen. The sodium sulfide is dissolved in alcohol and placed in



dinitrobenzene — *meta-nitraniline*

a steam-jacketed reducer; the dinitrobenzene is added either solid, or also dissolved in alcohol. The mixture is maintained at boiling temperature for two hours; then the alcohol is distilled off, condensed and collected in a similar reducer and is ready for the next batch; the loss of alcohol is slight.

There remains in the first reducer the meta-nitraniline mixed with the inorganic salt; the mass is agitated with water which dissolves the salt. The suspension is pumped into a filter press where the meta-nitraniline is obtained as a moist cake; it is dried on trays in a vacuum drier.

The isomer, para-nitraniline, is made by nitrating aniline after protecting the amino group by acetylation; in other words, by nitrating the white solid, acetanilide[6]; the temperature is maintained between 6° and 8° C.

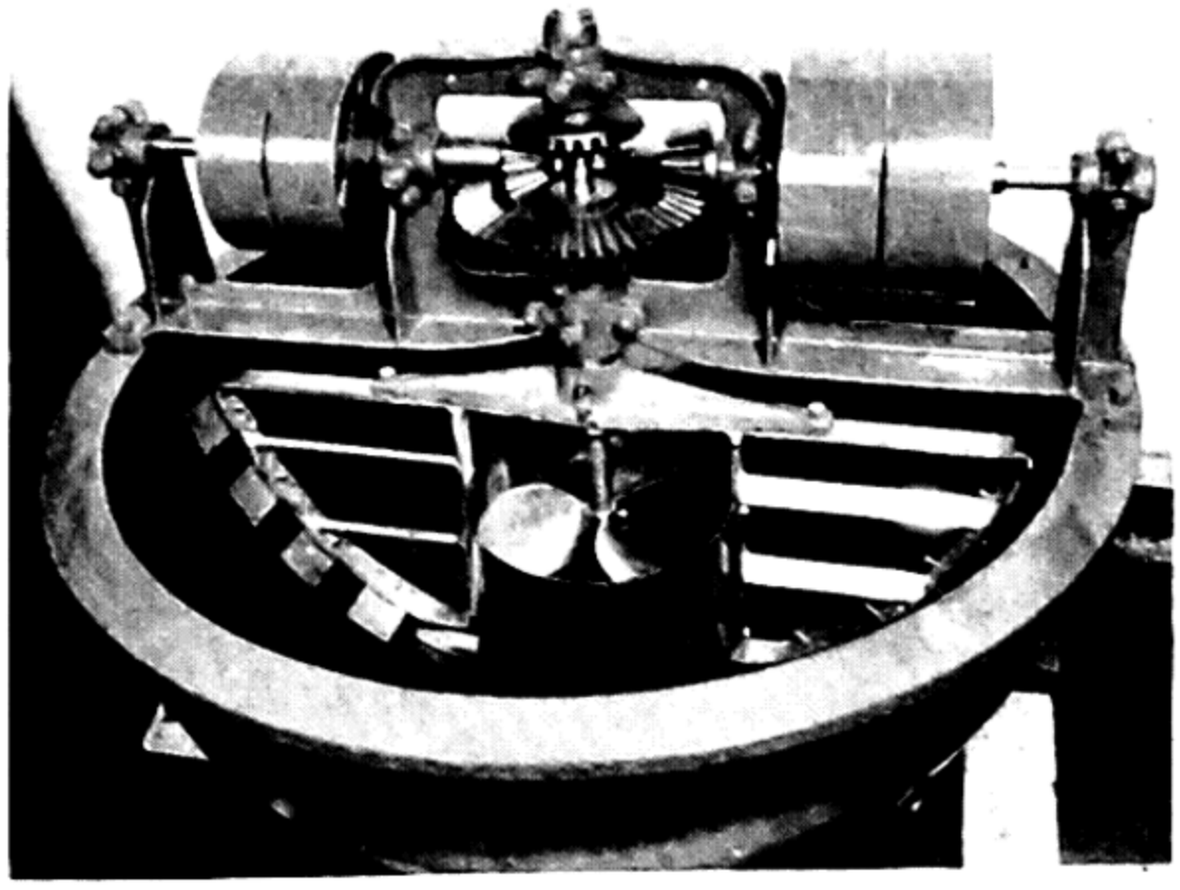


FIGURE 220.—A jacketed Dopp sulfonator, with scraper and propeller. Positive scraping of cooling of surface cuts in half the time required when using propeller only. Scraper on hollow shaft, low-speed; propeller on inner shaft, high speed.

SULFONATION

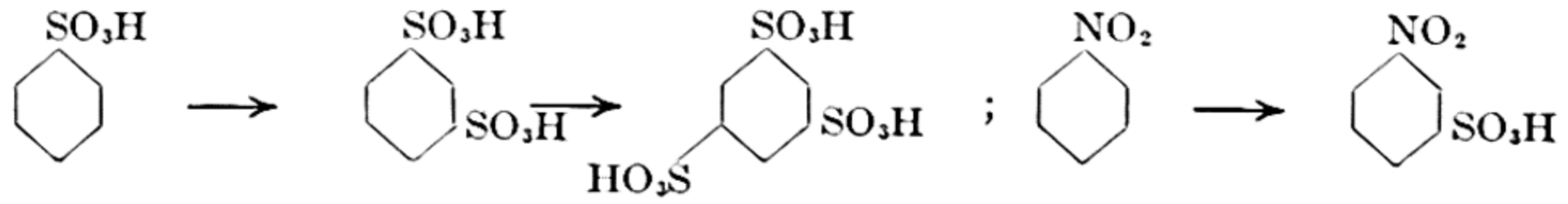
Sulfonation is performed to render insoluble compounds soluble in water or alkalies; or it may be performed as the first step in the introduction of the hydroxyl group, which is completed by subsequent alkaline fusion.

By direct sulfonation is meant the treatment of the substance with sulfuric acid; in the case of benzene, an oleum containing 8 per cent free SO_3 is added gradually, to offset the dilution caused by the water of reaction:

$$C_6H_6 + OHSO_3H \rightarrow C_6H_5 \cdot SO_3H + H_2O.$$

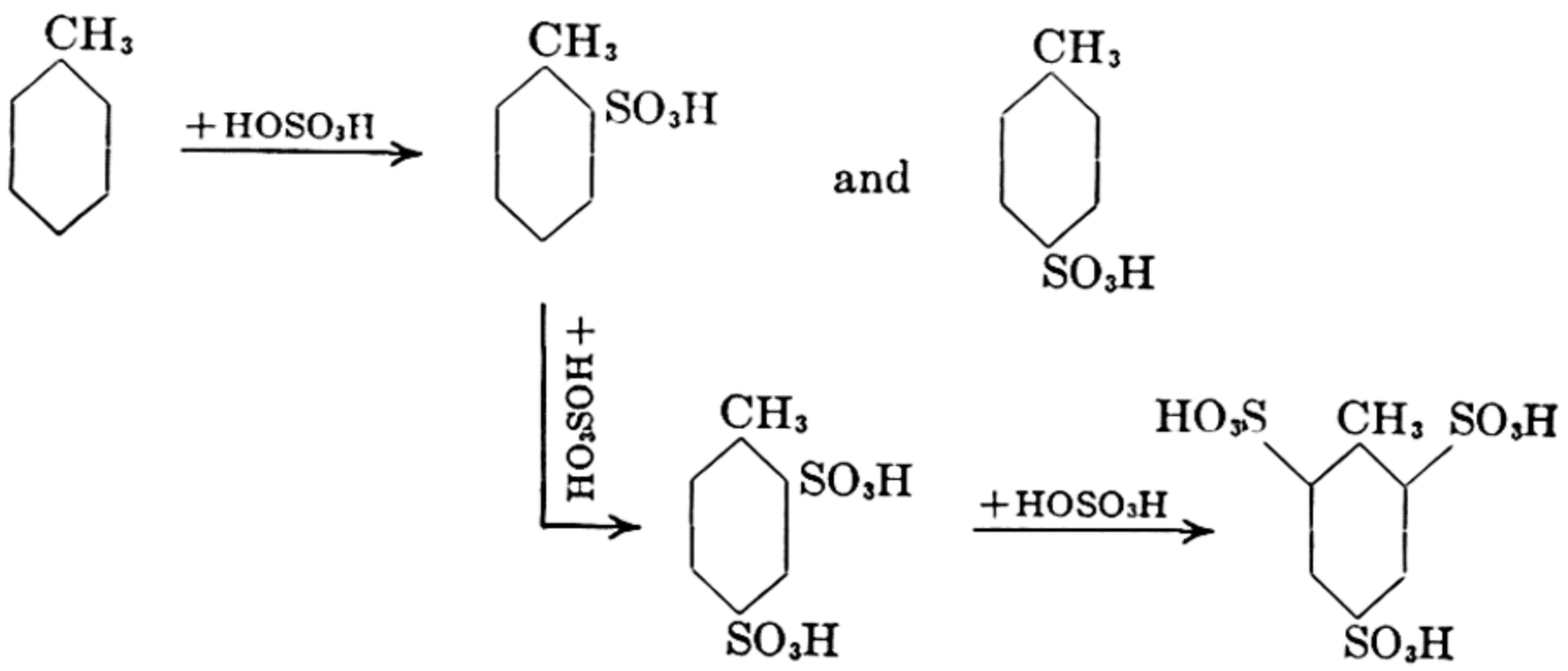
The temperature is maintained at 30° C. until near the end, when it is raised to 50°; the vessel used is shown in Figure 220. After the action is over, the charge is drowned in water, and the benzene sulfonic acid salted out; or, if the product is to serve for making phenol by alkaline fusion, lime is added; the free sulfuric acid is precipitated as sulfate which is removed by filtration. The liquor contains the calcium salt of the sulfonic acid; it is treated with soda ash, forming the sodium salt and precipitating calcium carbonate. After another filtration, the sodium salt in solution may be isolated by evaporation.

If there is present in the molecule one of the three groups, NO_2, COOH, or SO_3H, the entering sulfonic group will take the meta position, in accordance with the rule for orientation given under nitration:

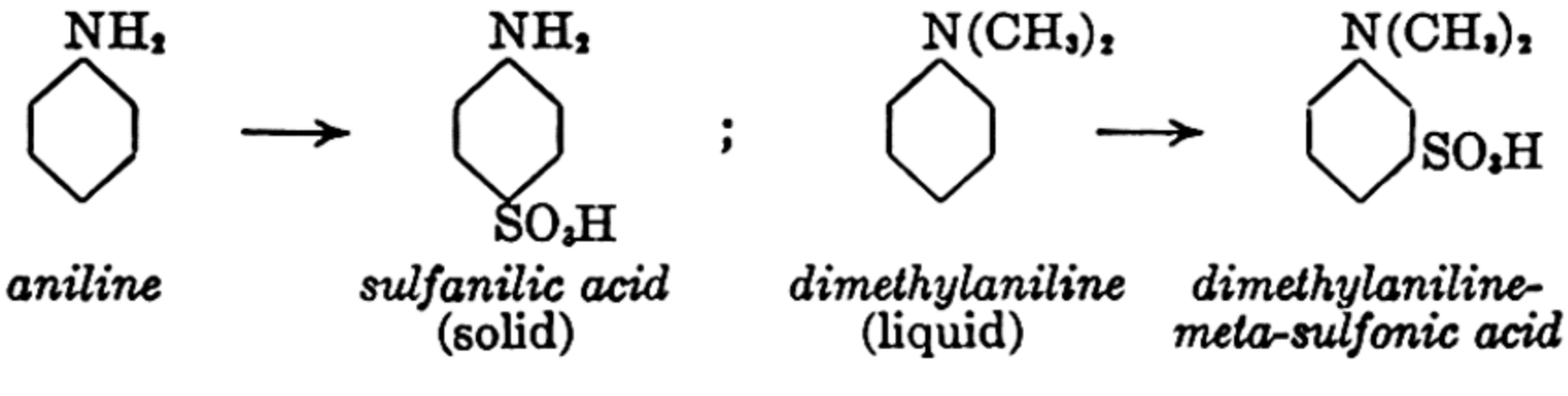


[6] Another method is given under Halogenation.

If the methyl group is present the result is different, but still in agreement with the rule; ortho and para derivatives are formed:

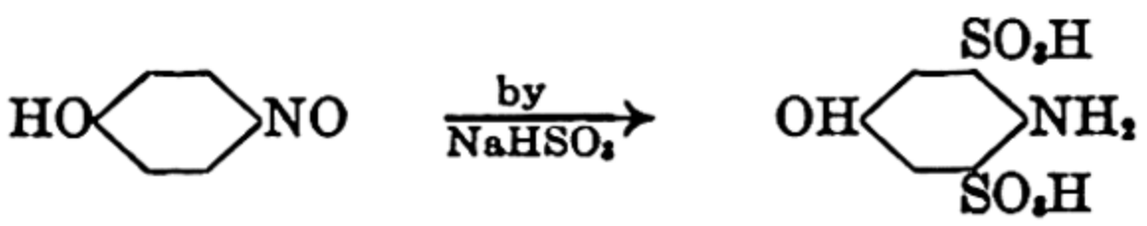


By sulfonating aniline, only para-sulfonic benzene, called sulfanilic acid, is formed; no protecting of the amino group is necessary; but if the aniline group is methylized, the sulfonic group enters meta:



aniline — *sulfanilic acid* (solid); *dimethylaniline* (liquid) — *dimethylaniline-meta-sulfonic acid*

Indirect sulfonation may be done in various ways; for instance, bodies with the quinonoid structure may be sulfonated by $NaHSO_3$, with simultaneous reduction of any nitroso or nitro group present to the amino group. Nitroso phenol is made by adding acid to sodium nitrite and phenol dissolved in caustic soda.



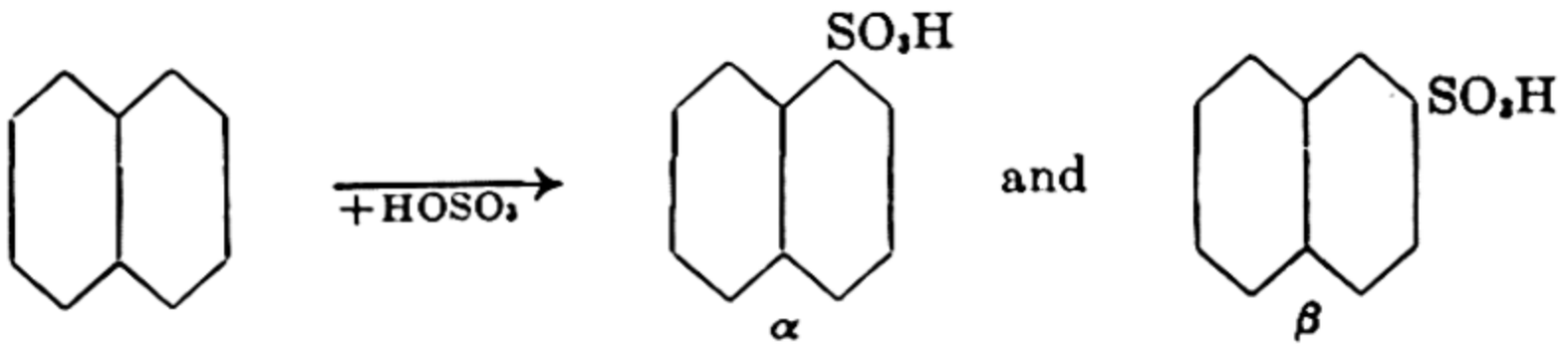
nitrosophenol — *disulfonic-para-aminophenol*

By reducing the same para-nitrosophenol with sodium sulfide (Na_2S), para-aminophenol is produced.

The sulfonation of naphthalene[7] leads to a large number of sulfonic derivatives. Making use of all sulfonating agents, there may be obtained 75 sulfonic acids, among which are 2 mono-, 10 di-, 14 tri- and 22 tetrasulfonic acids. The product obtained may be controlled, in some of the processes, by the choice of agent (sulfuric acid, oleum, chlorosulfonic acid and others); with any one agent, temperature and duration govern. Rarely is one single body produced free of isomers. The effort is rather to form a preponderant amount of one isomer. For example, for the monosulfonates, made by direct sulfonation with concentrated sulfuric acid, there are formed, at 80° C. and heating for 8 hours, 96.4 per cent of α-naphthalene

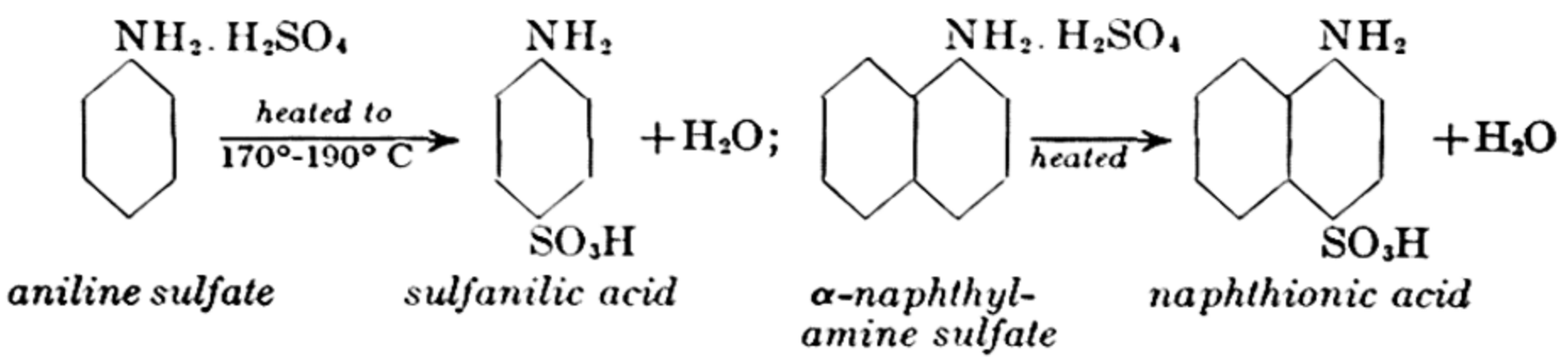
[7] "The organic chemistry of sulfur" (tetracovalent sulfur compounds), C. M. Suter. New York, John Wiley and Sons, 1944.

sulfonic acid. As the temperture is raised, correspondingly less of this isomer is formed, and more of the β isomer, until at 150° C., for example, 18.3 per cent of the α sulfonic acid is formed, and over 80 per cent of the β isomer. The sulfonation of naphthols and naphthyl amines similarly is a rich subject, requiring close study. The direct sulfonation of naphthalene to form the monosulfonic acid follows:

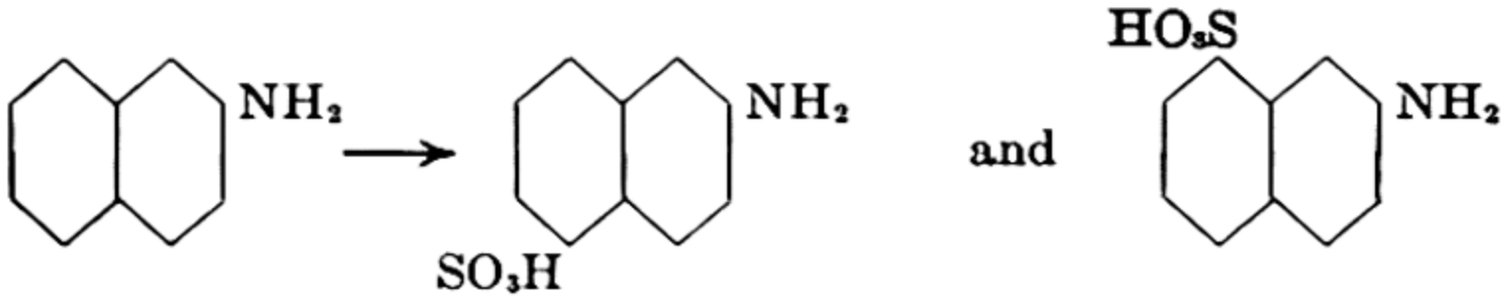


The naphthalene is melted and the acid run into it, to avoid the formation of disulfonic derivatives; the amount of acid is the calculated amount for one group. The water formed during the reaction retards but does not prevent it; a definite amount of oleum (8 per cent SO_3) is added toward the end in order to hasten it.

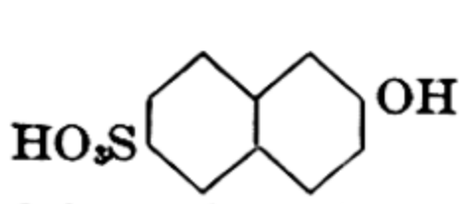
Sulfanilic acid and naphthionic acid are often prepared in an indirect way, namely, by forming the corresponding sulfate salt and heating the latter in thin layers, when an intermolecular change takes place and the sulfonic group enters the nucleus, in both cases in the para position; this is the "baking process."

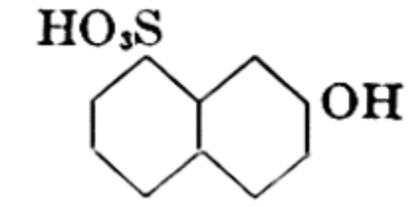


By direct sulfonation of α-naphthylamine, four of the seven possible α-naphthylamine sulfonic acids may be formed; the chief product under the proper conditions is the 1,4 isomer, naphthionic acid. β-naphthylamine, on direct sulfonation, forms chiefly a mixture of 2-5 and 2-8 sulfonic acids:



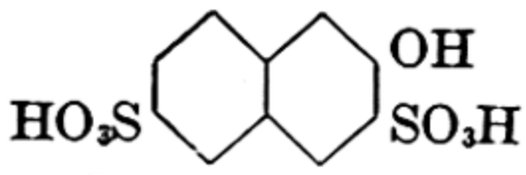
Two isomeric monosulfonic acids resulting from the sulfonation of β-naphthol are



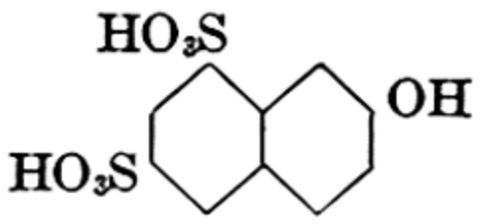


At lower temperatures, the 2,8 isomer is preponderant; at 110° C. (230° F.), the 2,6 isomer.

By further sulfonation, two isomeric disulfonic acids are the chief products: in the cold, preponderantly G acid forms, while at higher temperatures, the R acid forms in greater amount.



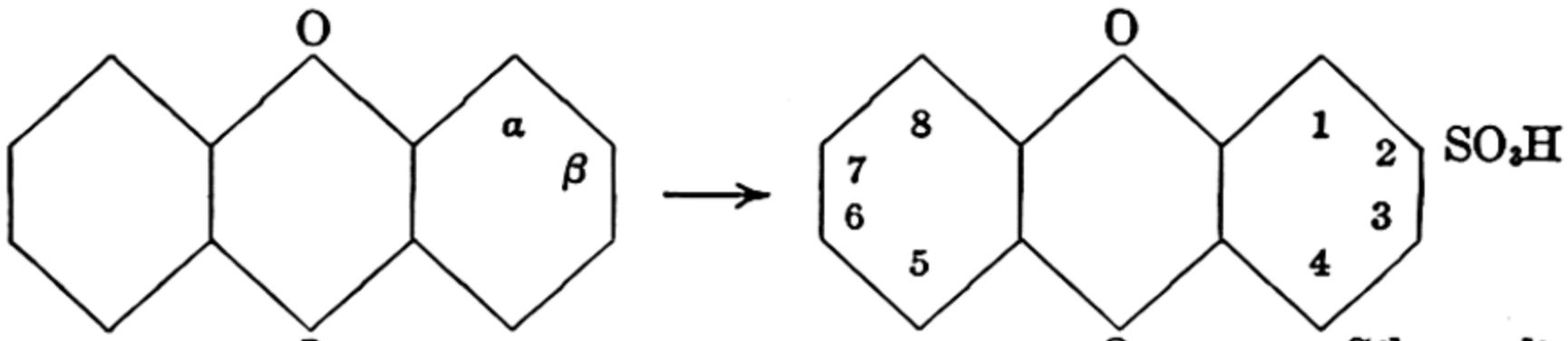
R acid (2–3–6)



G acid (2–6–8)

These two differ in that a diazo body couples with them at different rates; with the R acid, rapidly; with the G acid, slowly.[8] Schaeffer's acid and Crocein acid show the same difference.

Anthraquinone, a yellow solid, is sulfonated by suspending it in oleum containing 45 per cent free SO_3 (very strong oleum), and heating to 150° C. for one hour; the resulting melt is run into water and neutralized with caustic soda while hot. On cooling, the sodium salt of the β-sulfonic-anthraquinone separates as a salt resembling metallic silver. For that reason it is called silver salt, important chiefly in the manufacture of alizarine.



O O *Silver salt*

On further sulfonation, a mixture of the 2,6- and 2,7-disulfonic anthraquinones is formed.

If the sulfonation is performed in the presence of mercurous sulfate, different products are obtained: a single sulfonic group enters at α or 1; two groups enter to form the 1,5- and 1,8-disulfonic anthraquinones.

Halogenation

Of the three halogens, chlorine is the most widely used, because of its comparative cheapness. As a rule, chlorinations are performed by dried chlorine gas, that is, by direct chlorination, with or without a catalyzing agent.

Chlorobenzene is made by passing a stream of dried chlorine into benzene in the presence of 1 per cent ferrous chloride; some paradichlorobenzene is formed at the same time:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl, \text{ and}$$

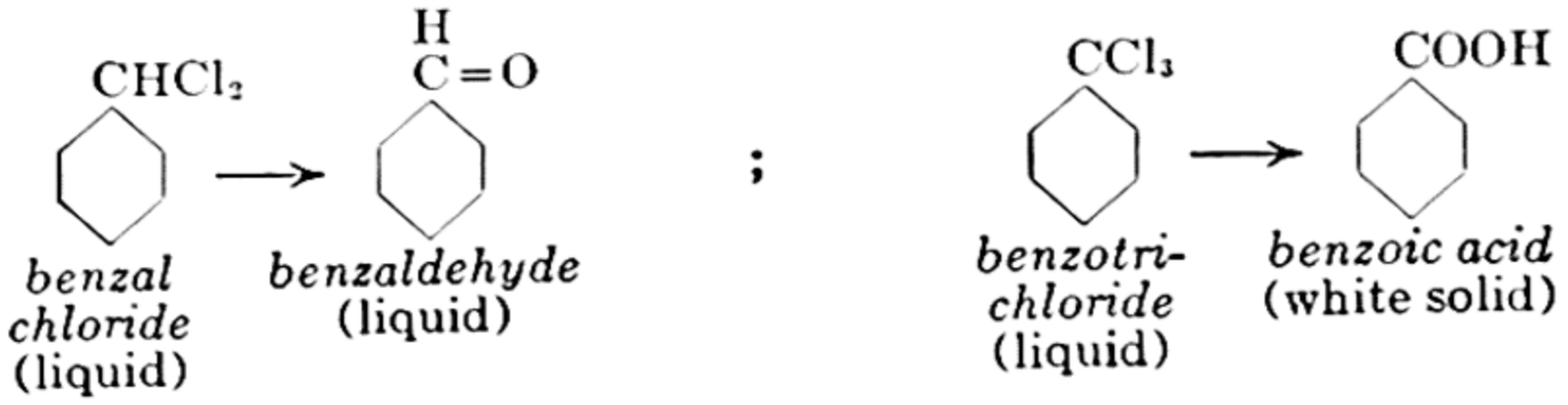
;

chlorobenzene (liquid)

paradichlorobenzene (white solid)

[8] R acid gives redder dyes, G acid gives dyes more on the yellow, hence the designations which come from the German "rot" and "gelb."

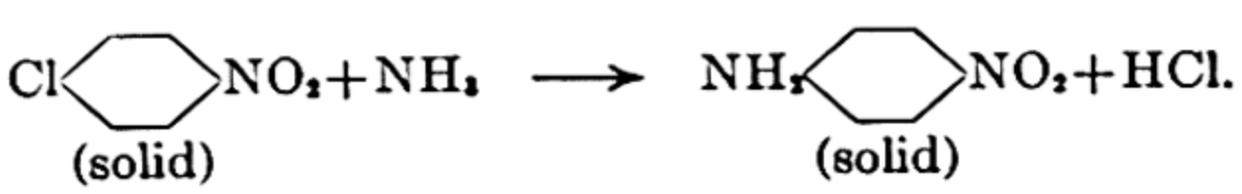
When passed into boiling toluene contained in a stoneware or enameled vessel, the chlorine enters the methyl group, producing a mixture of benzyl chloride $C_6H_5CH_2Cl$, benzal chloride, and benzotrichloride. Treated with water in the presence of calcium carbonate, benzal chloride gives benzaldehyde, while benzotrichloride under the same treatment gives benzoic acid.



In this chlorination an iron vessel cannot be used, for the iron would cause a portion of the chlorine to enter the nucleus.

There are many catalytic agents in use such as SO_2Cl_2 (sulfuryl chloride), PCl_5 (phosphorus pentachloride), $SbCl_5$ (antimony pentachloride), I_2 (iodine), Fe (iron); furthermore sunlight, ultraviolet rays, and temperature influence the course of the reaction.

By means of the halogen, the reactivity of the compound is increased; the chlorine is more or less readily replaced by other groups. In the benzene or naphthalene nucleus, the chlorine is the more easily replaced, the greater the number of negative groups, such as nitro groups, present. Thus with ammonia, chlorobenzene reacts, but with difficulty, while paranitrochlorobenzene reacts readily, forming para-nitraniline.



In acetic acid, one, two, or three of the hydrogen atoms in the methyl group may be replaced by direct chlorination of the warm liquid in the presence of sulfur:

$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH
mono-chloroacetic acid (solid)	*dichloroacetic acid* (liquid)	*trichloroacetic acid* (solid)

Alkylation

The alkyl groups, such as the methyl group, may be introduced into the amino group of an aromatic amine by heating it under pressure with methanol, in the presence of mineral acids.

$$C_6H_5 \cdot NH_2 + CH_3OH \longrightarrow C_6H_5 \cdot NH \cdot CH_3 + H_2O$$

aniline — *mono-methylaniline* (liquid)

Another method used at present is the treatment with methyl sulfate or ethyl sulfate in the cold, in presence of caustic soda:

$$C_6H_5 \cdot OH + (CH_3)_2SO_4 \longrightarrow C_6H_5 \cdot OCH_3 + H \cdot CH_3 \cdot SO_4$$

phenol — *methyl sulfate* — *anisole* — *methyl sulfuric acid*

Alkaline Fusion

By means of an alkaline fusion, a sulfonic group is replaced by a hydroxyl group; there are other methods of introducing the hydroxyl group, but this is the simplest. The sulfonic acid is dissolved in a concentrated solution of sodium hydroxide or caustic in a covered cast-iron pot provided with a scraping stirrer and heated externally by steam, oil bath, or an open fire. The water is evaporated, and on continued heating, the mass fuses; the temperature varies for the various reactions, but lies between 190° and 350° C.

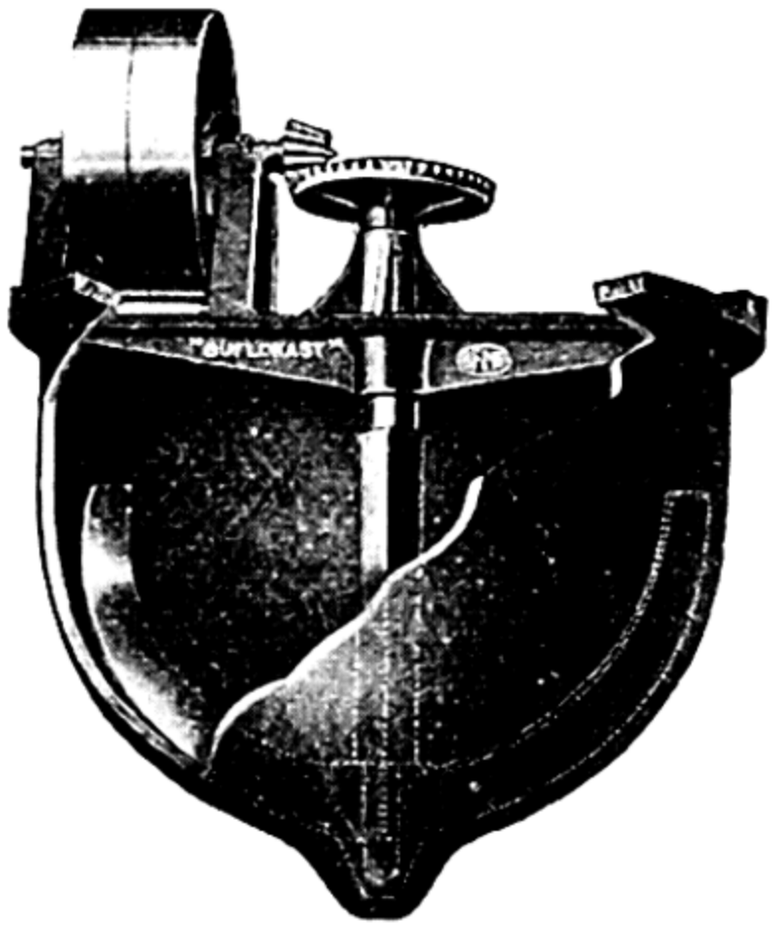
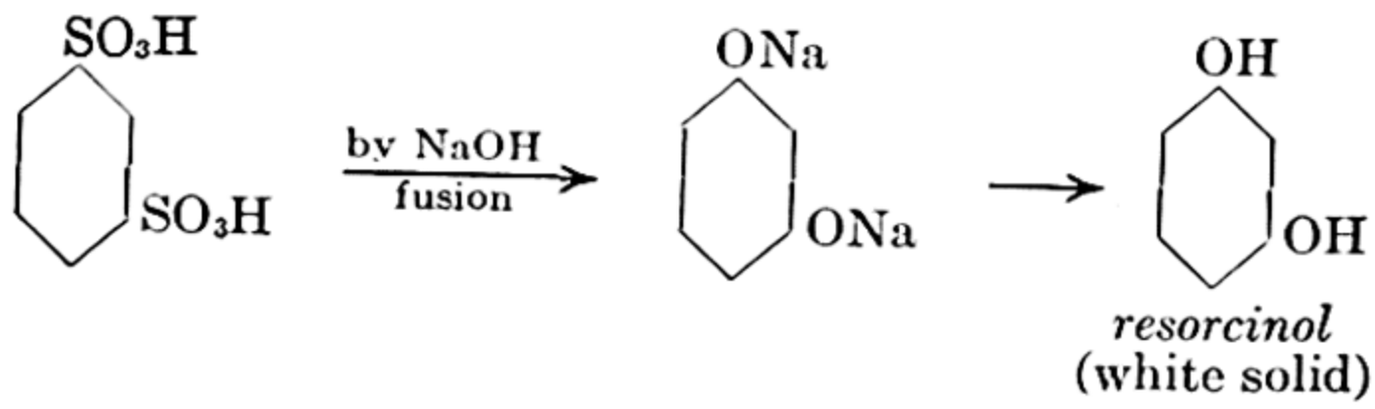


Figure 221.—Cast-iron fusion pot for alkaline fusions, with agitator.

Phenol is manufactured by fusing benzene sulfonic acid with caustic; this reaction as well as two others are discussed in Chapter 35.

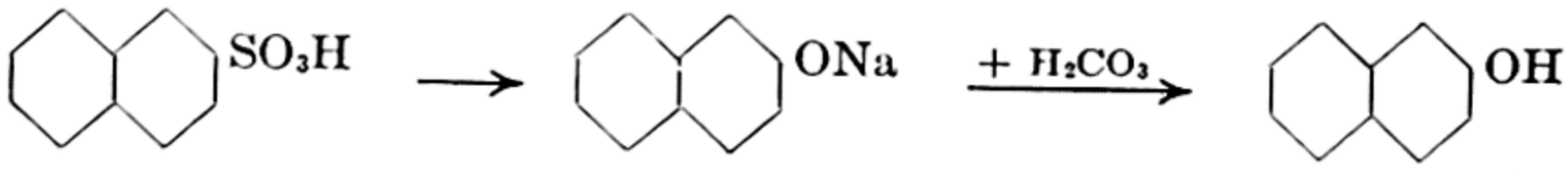
$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5 \cdot ONa + Na_2SO_3 + H_2O$$

The sodium phenolate formed is treated with acid to liberate the phenol. Resorcinol is made by alkaline fusion:



resorcinol
(white solid)

β-naphthol is made by fusing the corresponding sulfonic naphthalene with caustic; the naphtholate is treated with carbonic acid, and the precipitated β-naphthol is purified by distillation in vacuum.



β-naphthol
(solid)

α-naphthol is not made from the sulfonic derivative, because some of the β-naphthol is always formed at the same time; instead, α-naphthyl amine sulfate is heated with excess water in closed lead-lined vessels to 200° C. for two hours. On cooling the α-naphthol crystallizes out.

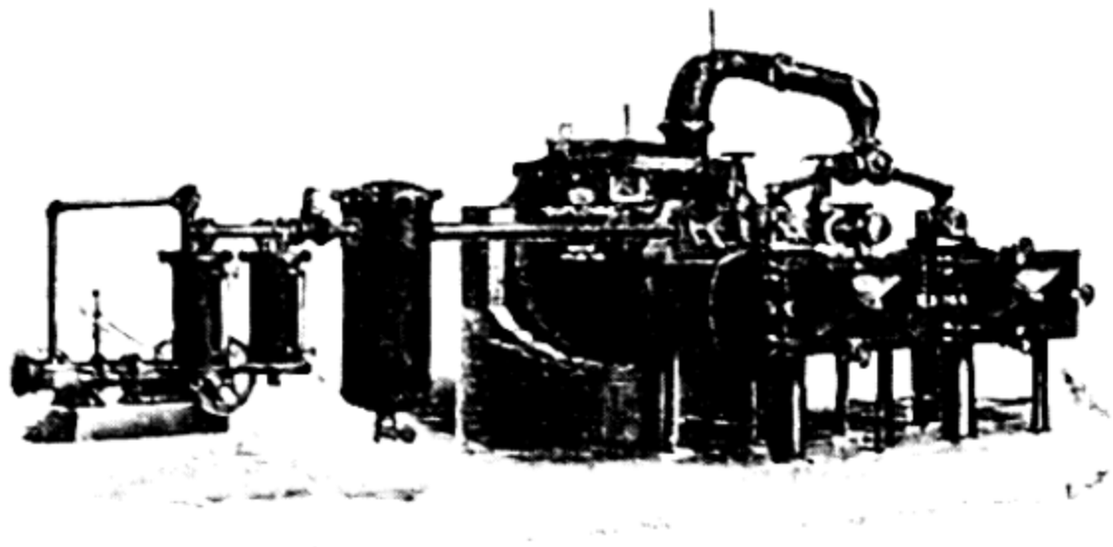
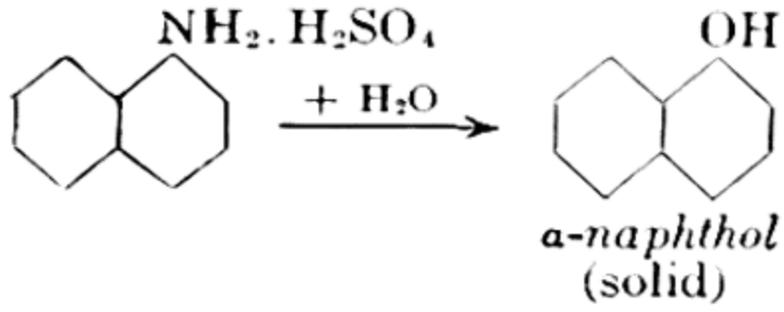
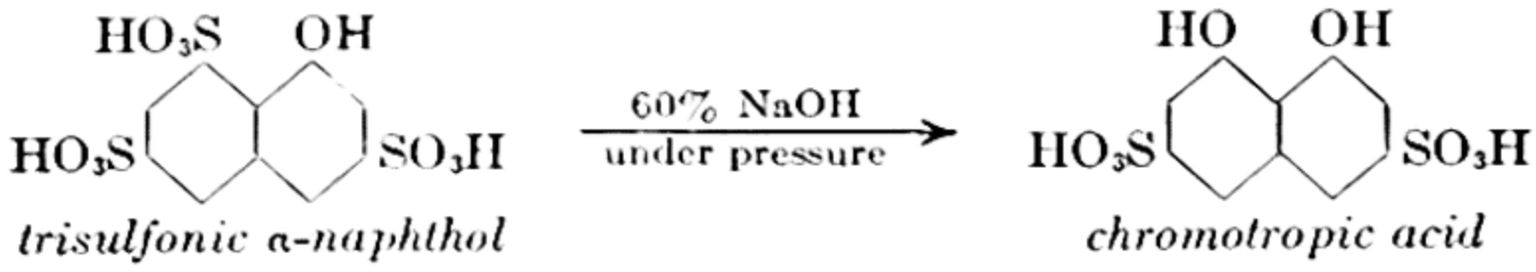


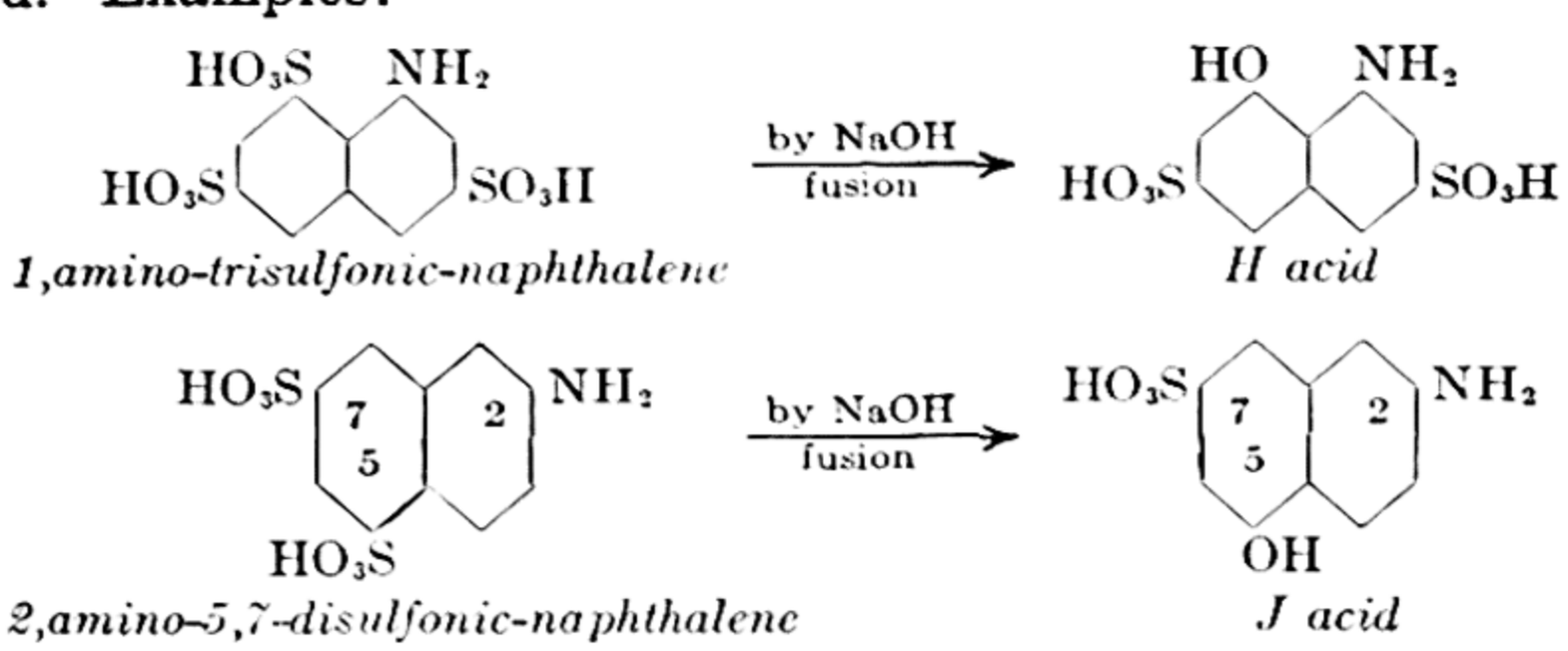
FIGURE 222.—A β-naphthol still. (Courtesy Buflovak Equipment Division, Blaw-Knox, Pittsburgh, Pa.)



Sometimes the action of the concentrated fused caustic is too great; in that case a water solution is used and the reaction mix heated under pressure:

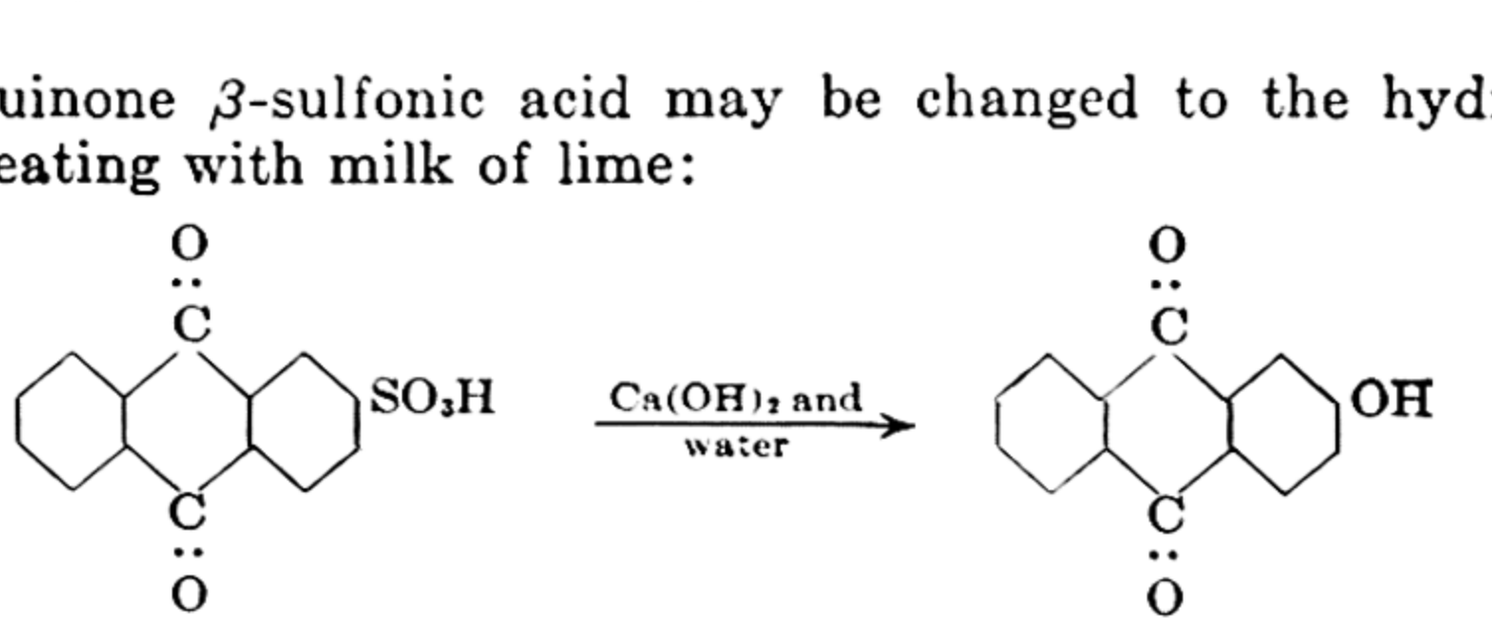


Sulfonated naphthyl amines may be fused with caustic to give aminonaphthols and aminonaphthol-sulfonic acids; the amino group is not destroyed. Examples:

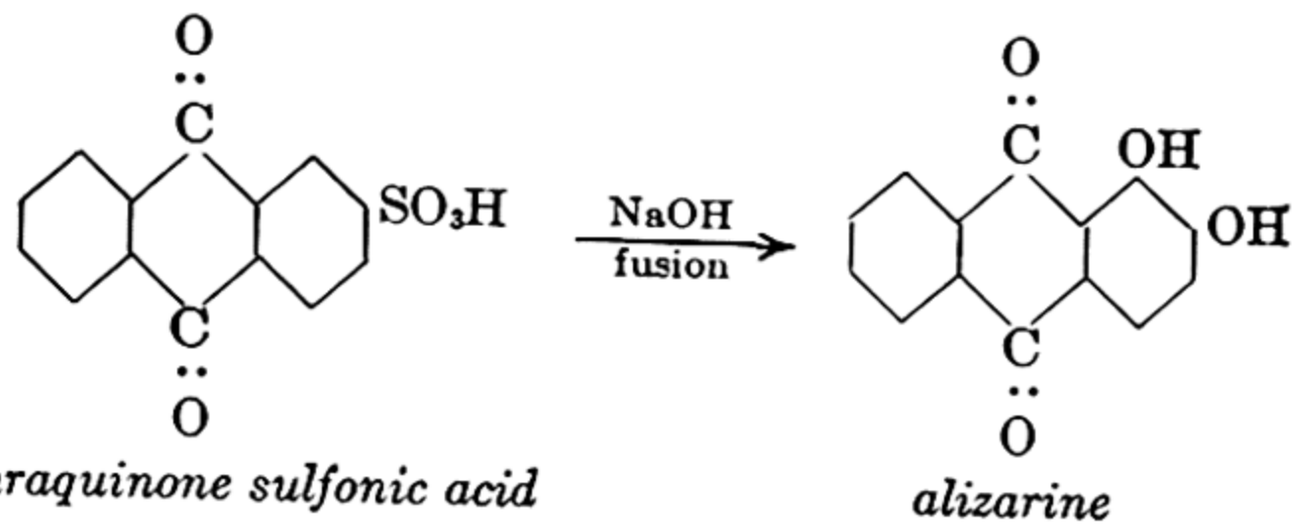


The aminonaphthol-sulfonic acids are almost indispensable for the manufacture of azo dyes; but while most of the important azo dyes contain the naphthalene residue, there are exceptions. Thus Wool Yellow X is an excellent example of important azo dyes which do not contain a naphthalene nucleus.

Anthraquinone β-sulfonic acid may be changed to the hydroxyl compound by heating with milk of lime:



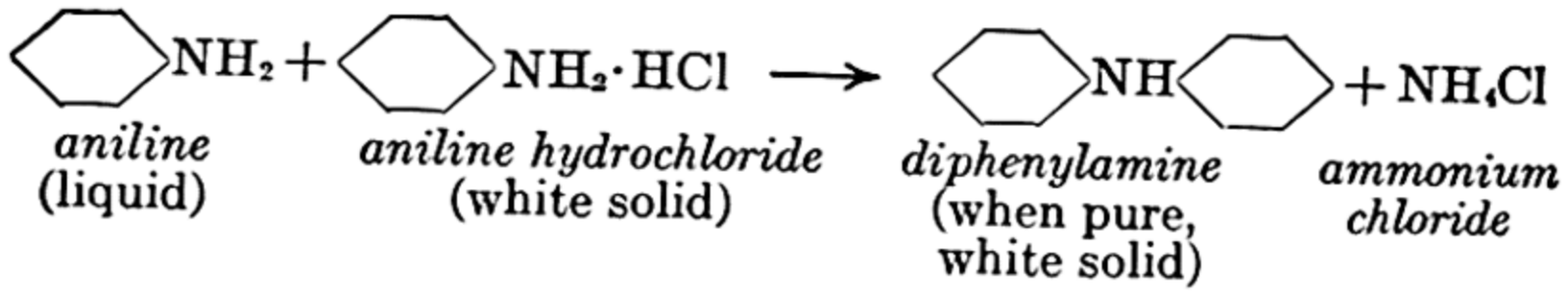
The same sulfonic acid fused with caustic gives the di-hydroxy derivative in addition to the mono-hydroxy compound. By adding an oxidizer such as potassium nitrate or chlorate, a high yield of the dihydroxy anthraquinone forms; this is alizarine, which is discussed further in the next chapter.



anthraquinone sulfonic acid — *alizarine*

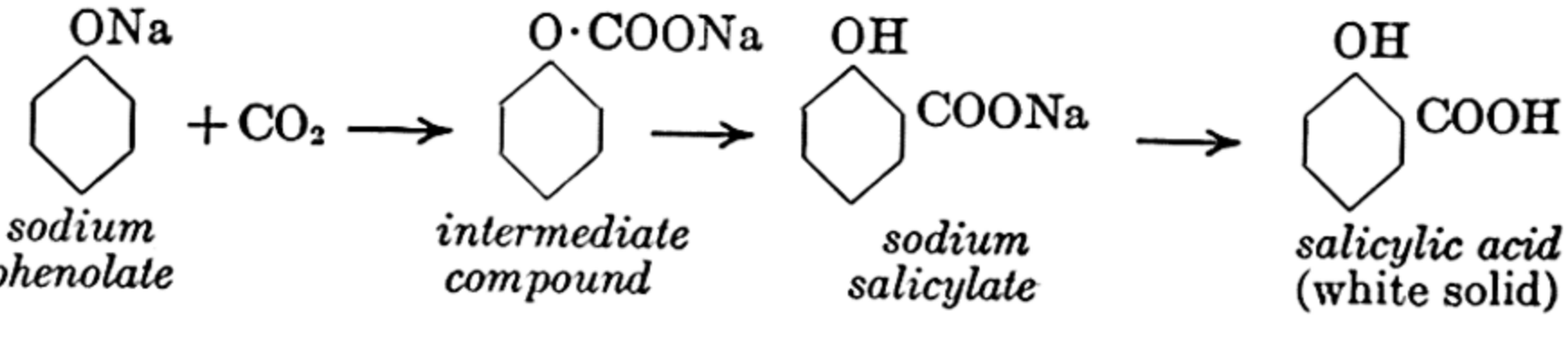
Other Important Intermediates

Diphenyl amine is made by heating aniline and aniline hydrochloride in a closed cast-iron vessel, an autoclave, for 32 hours at 200° C.; the melt is extracted with weak hydrochloric acid, and distilled under reduced pressure. This body is important not only as an intermediate but also as a stabilizer for gun-cotton.



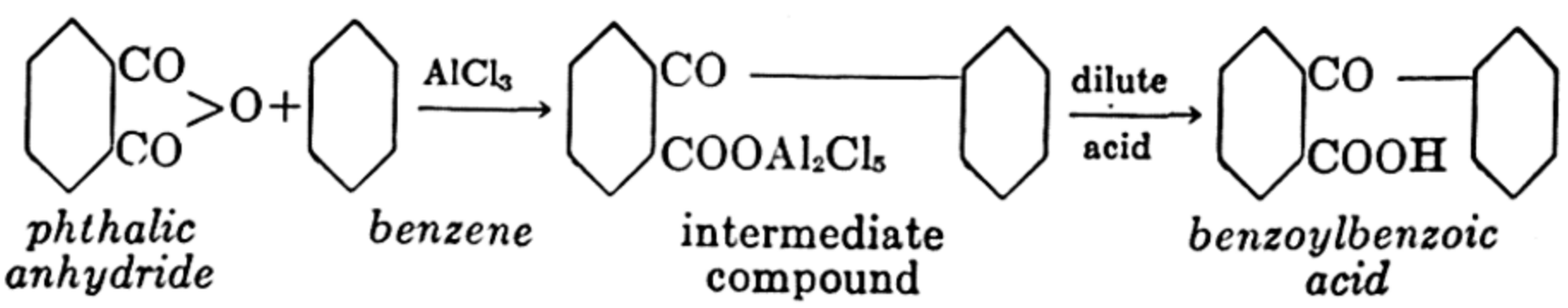
aniline (liquid) — *aniline hydrochloride* (white solid) — *diphenylamine* (when pure, white solid) — *ammonium chloride*

Salicylic acid is made by dissolving phenol in sodium hydroxide, evaporating to absolute dryness, passing in carbon dioxide under pressure, and maintaining the temperature near 150° C. in a cast-iron closed vessel. The charge is dissolved in water, and acidified to precipitate the free acid, which may be purified by distilling at low pressure.



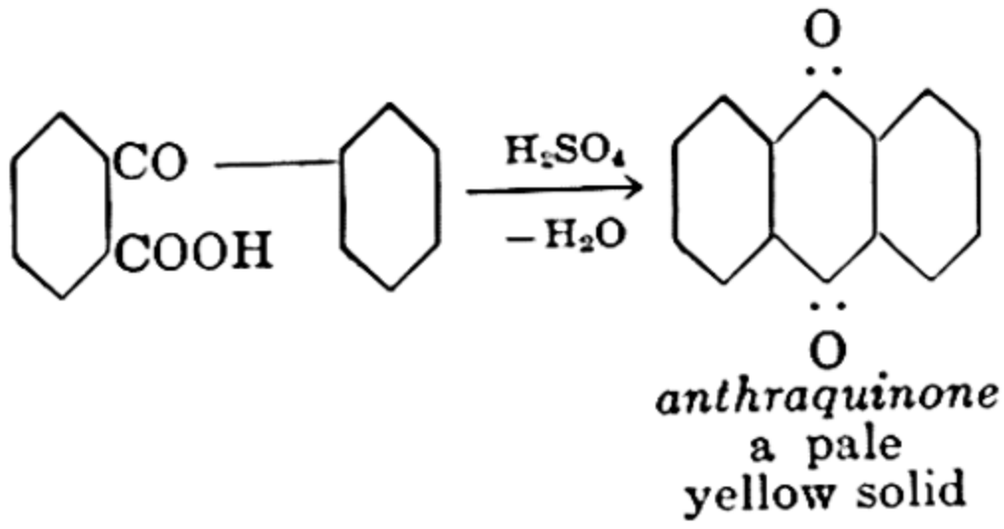
sodium phenolate — *intermediate compound* — *sodium salicylate* — *salicylic acid* (white solid)

The present method of making anthraquinone is as follows. Phthalic anhydride and benzene are heated in the presence of aluminum chloride, forming benzoylbenzoic acid:



phthalic anhydride — *benzene* — intermediate compound — *benzoylbenzoic acid*

When benzoylbenzoic acid is dehydrated by means of strong sulfuric acid, anthraquinone is formed:



anthraquinone
a pale
yellow solid

Production figures for some typical intermediates are given in Table 107.

TABLE 107.—*United States production of a few dye intermediates and of some raw materials.**

	1947 Pounds		1946 Pounds	
Nitrobenzene	142,198,000	0.07	115,109,000	0.07
Naphthalene solidifying 79° C.	94,739,000	.09	96,307,000	.08
Aniline oil	107,027,000	.12	88,366,000	.10
1-Chloro-2,4-dinitrobenzene	21,616,000	.14	11,796,000	.11
Acetanilide (techn.)	8,898,000	.21	6,994,000	.21
Dimethylaniline-N-N'	6,789,000	—	3,656,000	.21
1-Naphthylamine	—	.34	4,297,000	.29
H acid	4,959,000	—	3,893,000	—
p-Naphthionic acid	—	—	2,222,000	.42
Sulfanilic acid	2,938,000	—	2,787,000	—
m-Phenylenediamine	1,295,000	—	1,156,000	—
J-acid	835,000	2.09	835,000	1.98
1-Naphthol	453,000	0.57	886,000	0.81
Total intermediates, including phenol, styrene, phthalic anhydride, chlorbenzene (see elsewhere	2,618,771,000	0.13	2,547,485,000	0.11
	Gals.		Gals.	
Benzene (except motor benzene)	150,605,000	0.17	135,240,000	0.14
Toluene, from coal	27,322,000	0.19	24,184,000	0.21
Toluene, from petroleum	28,840,000	0.17	—	—

* U. S. Tariff Commission.

OTHER PATENTS

U. S. Patent 1,841,622, azo dye intermediates and the dyes therefrom; 1,834,876, production of dyestuff intermediates, di-anthraquinonyl derivatives containing chlorine, bromine and sulfonic acid groups in the 2-2 position; 2,029,315, trifluoromethyl-phenyl-azo-diamino pyridines and process for making same.

"Phthalocyanine derivatives as dye intermediates," Brit. Pat. 589,118 (C. A., 41, 7763).

PROBLEMS

1. 2500 pounds of benzene are nitrated in one batch, with a 90 per cent recovery, to nitrobenzene which is then reduced to aniline by Fe and HCl. The aniline recovery based on the nitrobenzene is 88 per cent. How much aniline is obtained? How much Fe and HCl will be required?

2. Diphenyl amine is made by the process given in the text. In order to produce 1200 pounds every day, how much of the two raw materials will be needed? The yield comes to 88 per cent. How much ammonium chloride will be left in the still?

From information obtained through the reading references, what size apparatus and what kind would you propose?

Reading References

"The manufacture of organic dyestuffs," André Wahl, translated from the French by F. W. Atack, London, G. Bell & Sons, Ltd., 1914.

"Aniline and its derivatives," P. H. Groggins, New York, D. Van Nostrand Co., 1924.

"Coal tar dyes and intermediates," E. D. B. Barnett in the series on Industrial Chemistry edited by Samuel Rideal, London, Baillière, Tindall & Co.

"Equipment for nitration and sulfonation," R. Norris Shreve, *Ind. Eng. Chem.*, 24, 1344 (1932).

"Intermediates for dyestuffs," A. Davidson, New York, D. Van Nostrand Co., 1926.

"The synthetic dyestuffs and the intermediate products from which they are derived," J. C. Cain and J. F. Thorpe, London, Chas. Griffin and Co., 1933.

"The insoluble azo (Azoic) colouring matters—Part I," S. Yates, *Ind. Chemist*, 20, 489 (1944) with a table of 30 "naphthols"; and Part II, p. 605, same year, with a table of 43 "bases" for azoic dyeings.

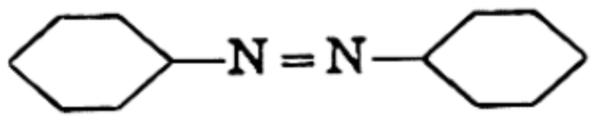
Natural dyes have been almost entirely displaced by synthetic organic dyes, which supply every shade imaginable, and which have a brilliancy never approached by natural dyes. The intermediates discussed in the previous chapter form the components of the artificial or synthetic dyes; how these component parts are assembled will be described in this chapter.

Chapter 28

The Manufacture of Dyes

An organic dye is a colored carbon compound which has the property of dyeing permanently, with or without mordant, animal, vegetable or artificial fibers. These dyes are derivatives of carbon-containing radicals in which at least one ring structure, such as the benzene or naphthalene nucleus, is contained. Other chemical elements are present in the dye molecule, such as hydrogen, oxygen, nitrogen, and sulfur.

There are several classes of dyes,[1] each of which contains one or more characteristic groups (a chromophore) such as $-N=N-$ for the azo class. The organic body containing the chromophore is a chromogen, such as azobenzene:



By introducing one or more of the following salt-forming groups (auxochromes), hydroxyl (OH), amino (NH_2), carboxyl (COOH), the chromogen becomes a dye.[2]

The shades and nuances of the dyes depend, (*a*) on the nature and number of the chromophore and salt-forming groups, (*b*) on the relative disposition of these groups within the molecule. The number of benzene and naphthalene groups and their relative configuration are extremely important.

Azo Dyes

Azo dyes contain at least one azo (diazo[3]) group, the divalent chromophore $-N=N-$ combined with two aromatic radicals. The simplest chromogen in this class is azobenzene, which has weak coloring power; on introduction of salt-forming groups, the coloring power increases.

[1] The classification scheme for the various chemical classes of dyes proposed in the revised Color Index is as follows: 1, Nitroso; 2, Nitro; 3, Monoazo; 4, Disazo, with 4 sub-groups: (a) primary disazo, (b) disazo from diamines, (c) secondary disazo, (d) tertiary disazo; 5, Trisazo; 6, Polyazo; 7, Azoic; 8, Stilbene; 9, Ketonimine and Azomethine; 10, Methine and Quinoline; 11, Triphenyl Methane and Diphenylnaphthyl Methane; 12, Xanthene, with 3 groups (Amino, Amino Hydroxy, and Hydroxy derivatives); 13, Acridine; 14, Thiazole (excluding Anthraquinone); 15, Indamine and Indophenol; 16, Azine; 17, Oxidation; 18, Oxazine; 19, Thiazine; 20, Sulphur; 21, Hydroxyketone, Hydroxyquinone, Hydroxylactone; 22, Anthraquinonoid, with 3 groups (Amino, Amino Hydroxy, and Hydroxy derivatives); 23, Anthraquinonoid and Polycyclicquinonoid Vat Dyes with sub-groups yet to be determined; 24, Indigoid and Thioindigoid; 25, Phthalocyanines; 26, Natural Organic Dyes with 2 sub-groups: (a) natural organic dyes, (b) lakes of natural organic dyes; 27, Natural and Artificial Inorganic Pigments.

[2] The hydroxyl and carboxyl form a sodium salt with caustic soda or soda ash, while the amino group forms a hydrochloride with hydrochloric acid.

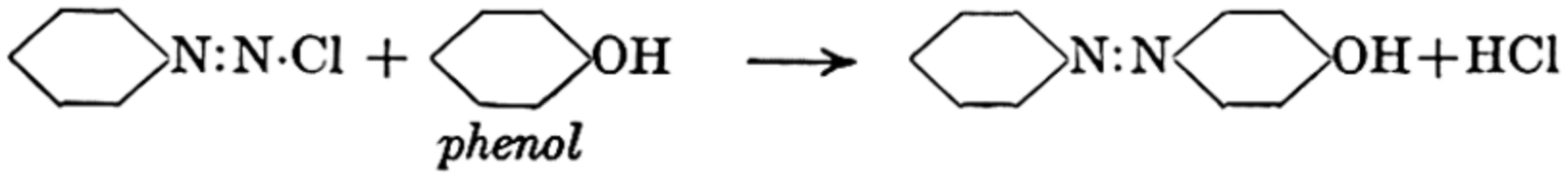
[3] Diazo means two nitrogens, from azote, the French word for Nitrogen. Diazo is contracted to azo, so that this latter expression also means two nitrogens in the form of $-N=N-$.

The main method [4] of formation of diazo substances is by the "diazotization" of primary amines, followed by "coupling" with hydroxy or amino derivatives of benzene or naphthalene which may also contain various other groups such as alkylalkoxy, halogen, sulfonic and carboxylic acid and others. Diazotization takes place when nitrous acid, HNO_2, reacts on the primary amine group, NH_2, attached to the benzene, naphthalene, or certain other nuclei usually in the presence of hydrochloric or sulfuric acid. Inasmuch as nitrous acid is unstable, its sodium salt, $NaNO_2$, is used, with an extra amount of hydrochloric acid.

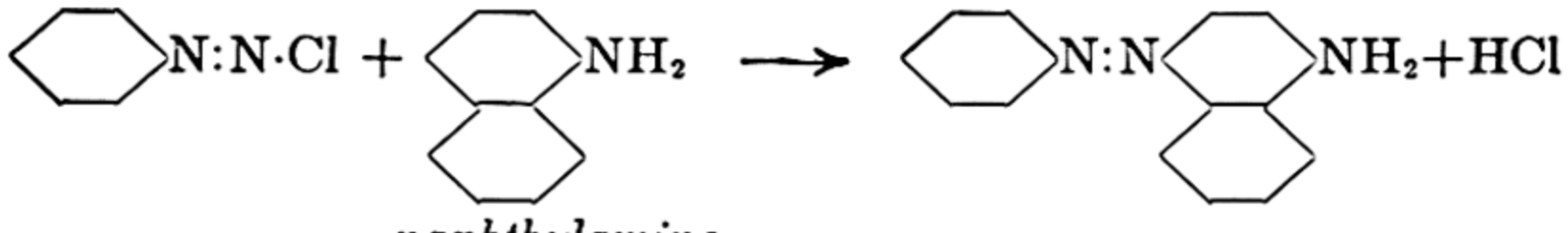
$$C_6H_5\cdot NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5-N=N-Cl + NaCl + 2H_2O$$

benzene diazonium chloride

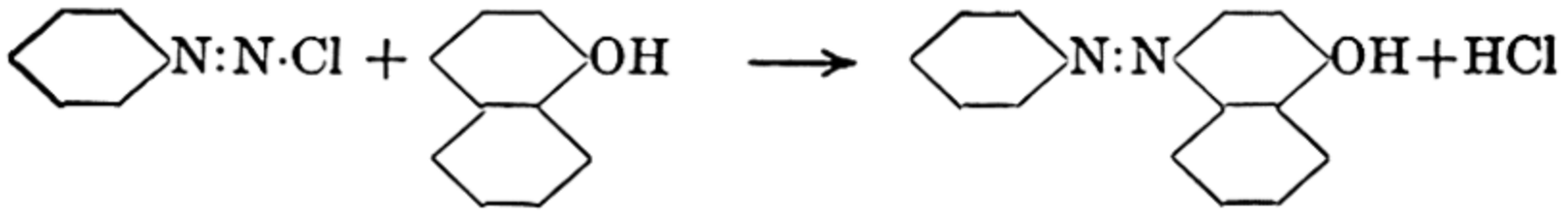
Examples of coupling reactions with benzene and other diazonium chlorides:



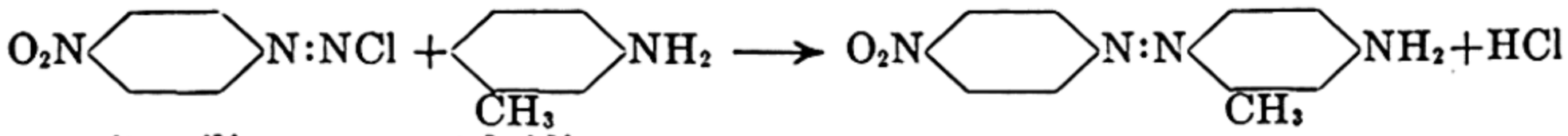
phenol



α-naphthylamine



α-naphthol



p-nitraniline *m-toluidine*

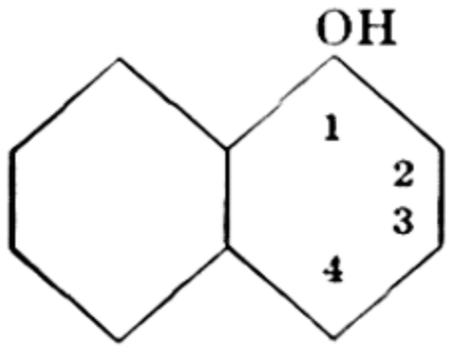
It will be noticed that the compounds with which the benzene (or phenyl-) diazonium chloride reacts contain the salt-forming groups, OH or NH_2. It is this property, possessed by the diazonium grouping, of combining with aromatic compounds containing one of these two salt-forming groups, which renders possible the formation of the numerous azo dyes. Certain general considerations may well precede the reactions for dye formation.

The diazo group does not enter at random, but in certain definite positions. The attack is generally in the nucleus, and one molecule of hydrogen chloride is eliminated. For the benzene derivatives, the attack is on the hydrogen para to the salt-forming group, or if that is occupied, in the ortho position; never in the meta position. Coupling in alkaline solution is rapid; in acid solution, slow. The alkaline solution must be used for phenol and substituted phenols, in order to form a solution; they are (mostly) not soluble in water. The acid solution must be used for aniline and other amines, again in order to bring them in solution. The alkaline solution re-

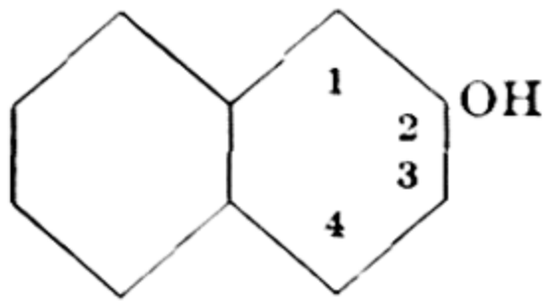
[4] Other methods are the reduction of nitro derivatives, and the action of a nitroso body on a primary amine.

moves the hydrogen chloride generated by the reaction as fast as it is formed. In the acid solution, such removal does not take place, unless sodium acetate is added, as is usually done; the reaction is sometimes hastened by the addition of soda ash.[5]

In the naphthalene derivatives, the orientation of the entering group is somewhat different. In α-naphthol, the attack is at 4, or para; if 4 is occupied, the diazo group enters at 2, or ortho; as this is in agreement with the rule for benzene derivatives, it may be considered normal. In β-naphthol, the coupling takes place at 1; never at 3 and never at 4. The naphthols are coupled in alkaline solution.



α-naphthol



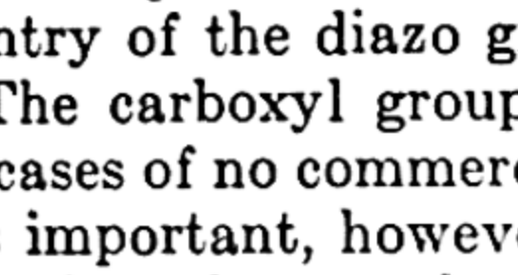
β-naphthol

The same position is taken by the diazo group when NH_2 replaces the hydroxyls; the substance is then a naphthylamine, and the coupling is performed in acid solution.

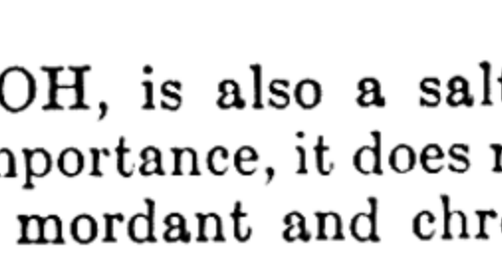
The sulfonic group, SO_3H, is also a salt-forming group, but it does not have the power, when alone, to cause coupling. In the naphthalene derivatives the presence of the sulfonic group in some cases influences the place of entry of the diazo group.

The carboxyl group, COOH, is also a salt-forming group; except in a few cases of no commercial importance, it does not cause coupling when alone. It is important, however, in mordant and chrome dyes, when the carboxyl group is ortho to a hydroxyl. Furthermore, amino compounds containing a carboxyl group ortho to the amino group, for example, anthranilic acid, are often used in chrome dyes.

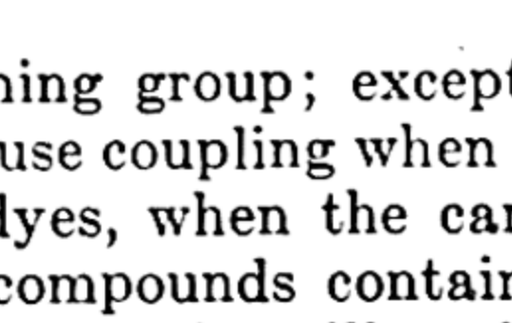
Certain aminonaphthol sulfonic acids couple twice, and in this case, the place of entry depends upon whether the coupling is performed in acid or alkaline solution. If acid, the coupling is ortho to the amino group; if alkaline, ortho to the hydroxyl. In the three samples following, the place of entry for acid coupling is marked X; for alkaline coupling, Z.



H acid[6]



Gamma acid

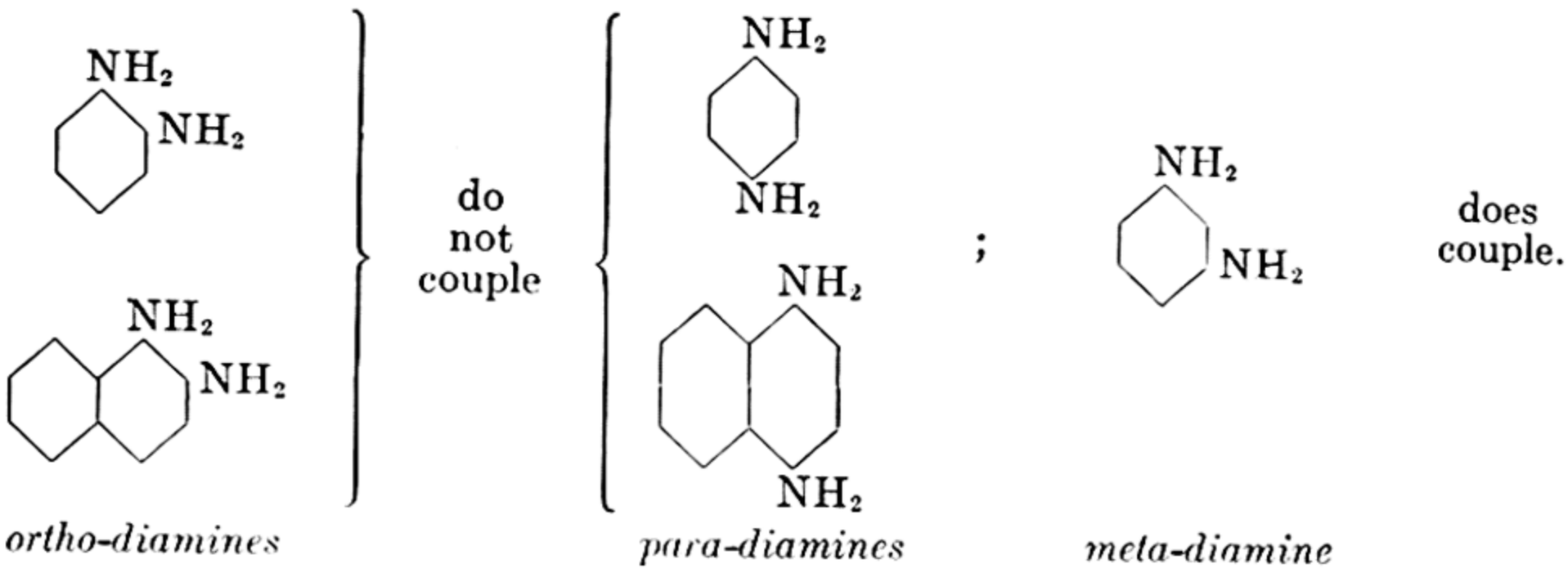


I acid

[5] There are numerous exceptions to these generalizations. For example, an acid coupling to metaphenylenediamine is likely to be more rapid than an alkaline coupling to phenol, while with some diazo compounds, phenol derivatives are advantageously coupled in weak acid medium.

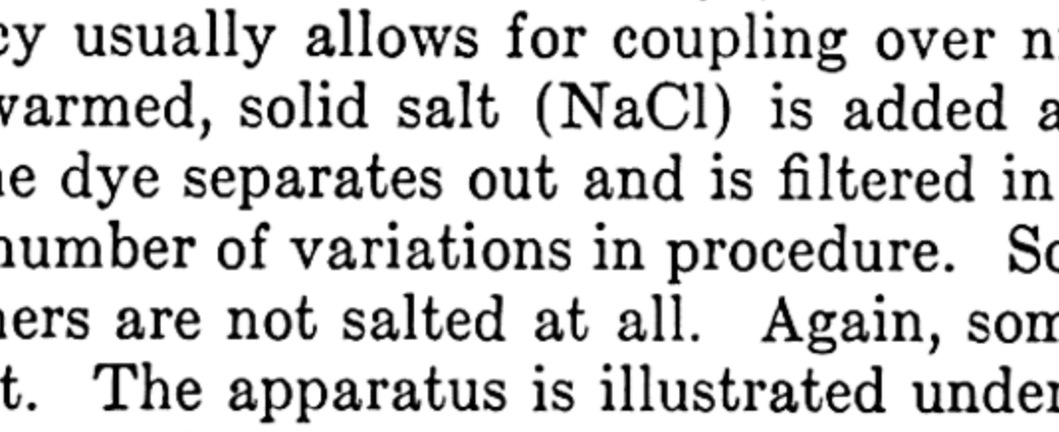
[6] It is recommended that the reader enter the formulas and names of the more important intermediates on a 5″ x 8″ card, and that he place this card next to the book while reading this chapter.

For these intermediates, too, alkaline coupling is rapid, acid coupling slower. Ortho- and para-diamines in both the benzene and naphthalene series do not couple at all; only the meta-diamines do so.



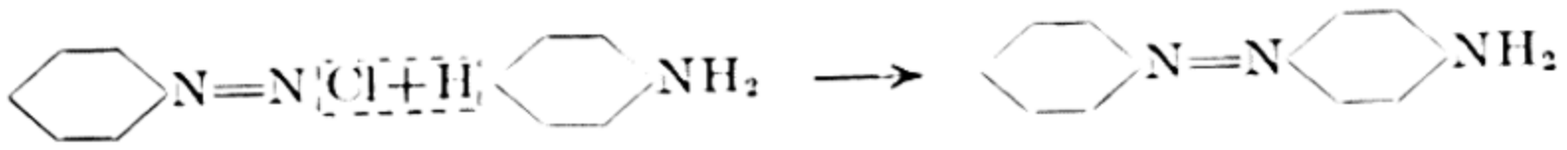
One procedure for diazotizing is to add at a slow rate a measured solution of sodium nitrite to the acid solution of the primary amine, in a wooden vat provided with an agitator. By means of direct ice addition, the temperature is kept low, usually 0° to 5° C.; generally a solution results. There are other procedures. Thus, solid sodium nitrite is often added; or sodium nitrite is added to the solution of the amino sulfonic acid and the two run into the acid solution. Some diazotizations are performed at higher temperatures. Generally, the diazonium compound is not isolated, but the solution is run at once at a slow rate into the alkaline (or acid) solution of the intermediate with which the diazonium compound is to be coupled. After the addition of the diazonium compound, the batch is agitated for a period varying between a few minutes and 3 days, until coupling is complete. Operating expediency usually allows for coupling over night. The solution in the dye is then warmed, solid salt (NaCl) is added and allowed to dissolve; on cooling, the dye separates out and is filtered in a plate-and-frame press. There are a number of variations in procedure. Some dyes are salted cold, while some others are not salted at all. Again, some dyes are filtered hot, after salting hot. The apparatus is illustrated under Benzidine.

Many of the compounds named in this chapter are described in the previous one and may be looked up there; the formulas of others are given at the proper place. It will be remembered that each corner of the benzene hexagon represents CH; where coupling has taken place, the hydrogen has been lost in the formation of hydrogen chloride, and its place taken by the diazo group. The full formula of the first azo dye, Spirit Yellow, given in the next division, is therefore:



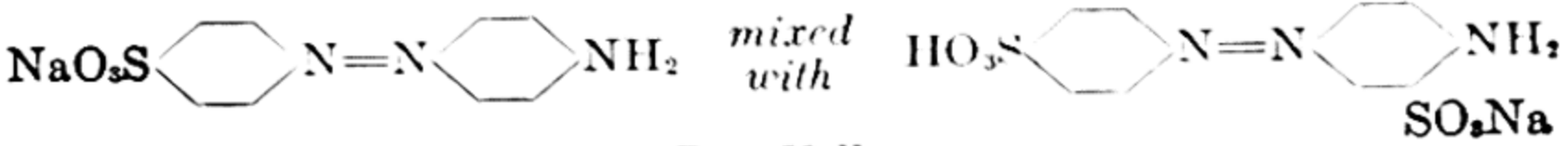
Mono-Azo Dyes. The mono-azo dyes contain the group $-N=N-$ once; the simplest example is aminoazobenzene, "Spirit Yellow," soluble in oil and

in alcohol; its use as a textile dye is unimportant. It is made by coupling benzene diazonium chloride with aniline in acid solution [7]:



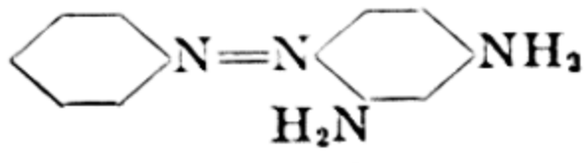
Spirit Yellow

On sulfonating it with fuming sulfuric acid, Fast Yellow is formed, which is a mixture of the mono- and di-sulfonic derivatives:



Fast Yellow

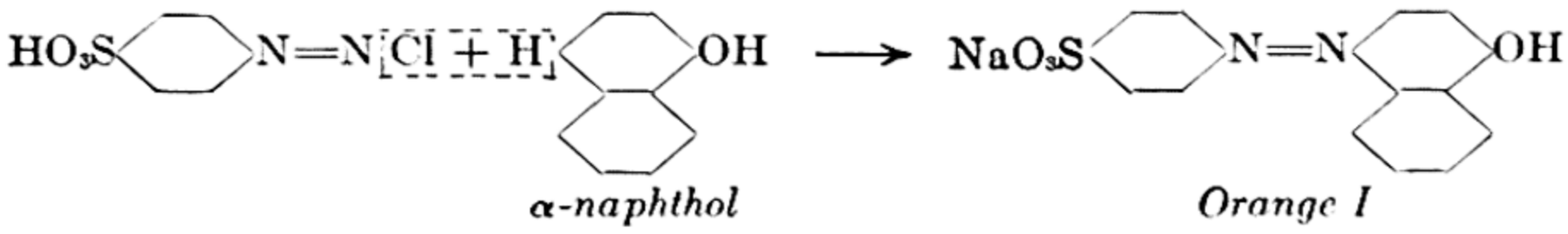
Benzene diazonium chloride coupled (acid) with meta-phenylene diamine gives Chrysoidine, which dyes a brown-yellow. The benzene diazonium chloride, it will be remembered, is made by diazotizing aniline.



Chrysoidine

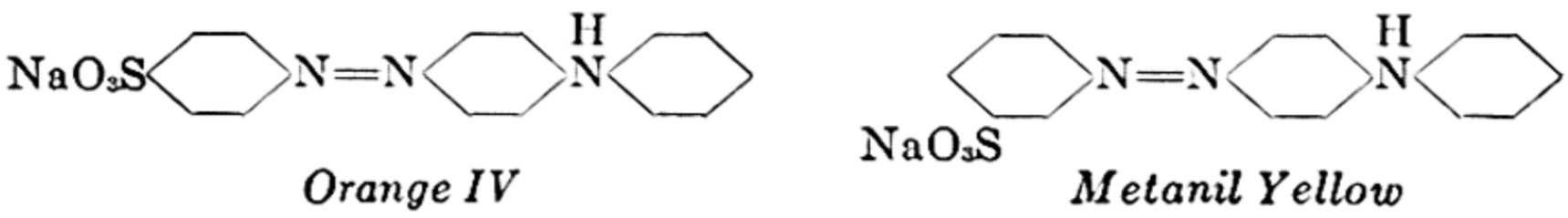
Sulfanilic acid

diazotized gives *p*-sulfophenyl diazonium chloride which may be coupled (alkaline) with α-naphthol to form Orange I.



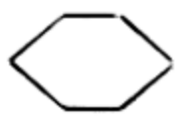
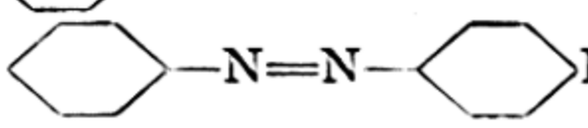
α-naphthol *Orange I*

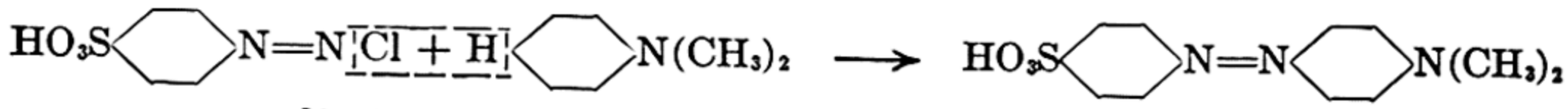
If instead of α-naphthol, diphenylamine is used, Orange IV results. Metanil Yellow is an isomer of Orange IV; it is made in the same way, except that metalinic acid is the body which is diazotized.



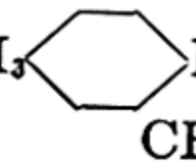
Orange IV *Metanil Yellow*

If sulfanilic acid is diazotized and coupled with dimethyl aniline, Methyl Orange or Helianthine is obtained.

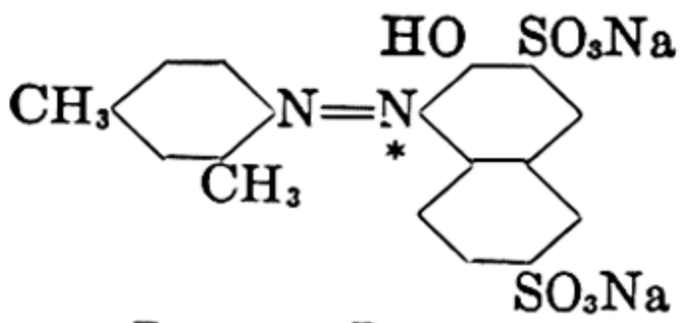
[7] An intermediate step is omitted; there is first formed diazoaminobenzene  and this rearranges itself under the influence of the acid into aminoazobenzene  .



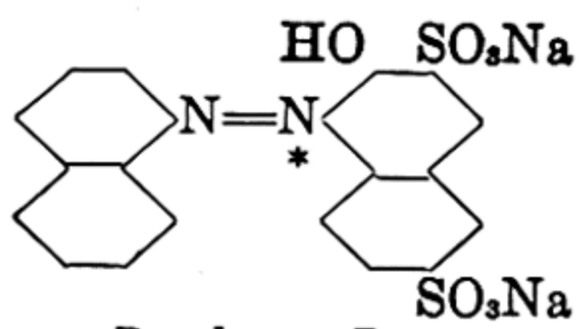
para-sulfonic diazonium chloride (from *sulfanilic* acid) + *dimethyl aniline* → *Methyl Orange*

Meta-xylidine,  , diazotized gives the corresponding di-

methyl-benzene-diazonium chloride; if the solution is run into an alkaline solution of R acid, Ponceau R, a wine-red dye, results. To avoid writing formulas twice, only the formula of the dye will be given, but the place of entry will be marked by an asterisk; this will make it easy to recognize the component parts of the dye. It will be understood that a molecule of HCl was formed and removed at the place marked.* Bordeaux B, which dyes a purer red, consists of diazotized α-naphthylamine coupled (alkaline) with R acid.

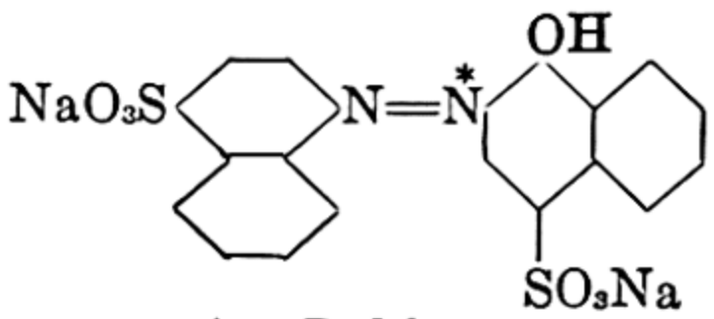


Ponceau R

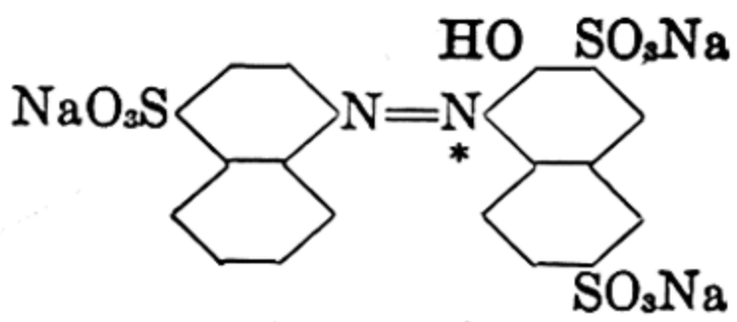


Bordeaux B

Azo Rubine is made from diazotized naphthionic acid, coupled (alkaline) with Nevile and Winther's acid. Amaranth contains naphthionic acid again, but this time coupled (alkaline) with R acid

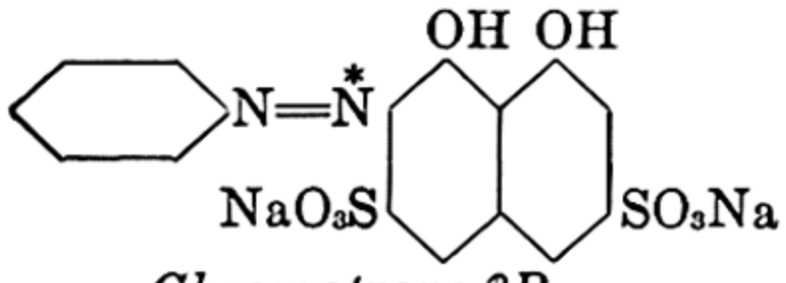


Azo Rubine

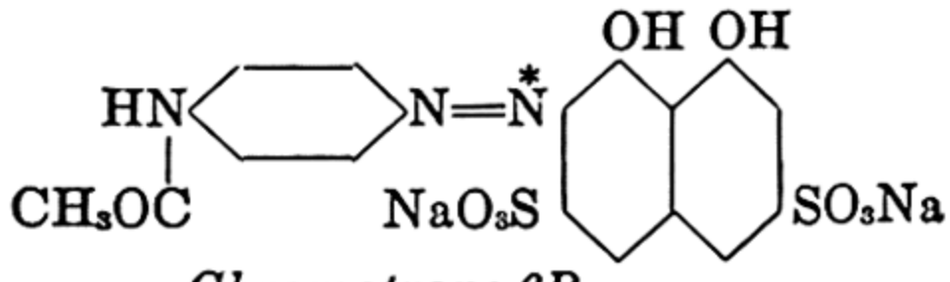


Amaranth

Chromotrope 2R consists of diazotized aniline coupled with chromotropic acid; Chromotrope 6B is *p*-aminoacetanilide coupled with the same chromotropic acid.



Chromotrope 2R

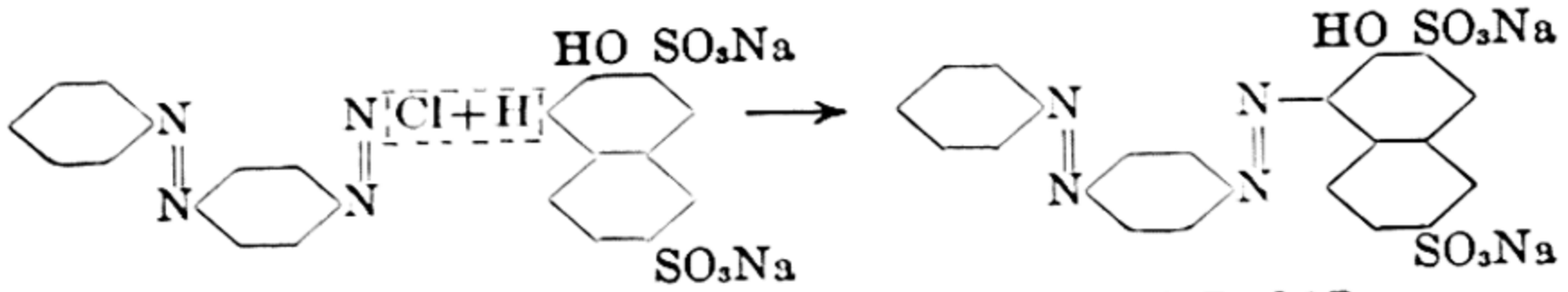


Chromotrope 6B

Secondary Dis-Azo Dyes. If an azo dye has been made with an intermediate which contains a free primary amine group, this group may be rediazotized by treating the azo dye with sodium nitrite solution and hydrochloric acid; the resulting diazonium compound may then be coupled to a new intermediate, and a dye will result which contains two azo groups. Such a dye is a dis-azo dye, and, when prepared in this way, it is a secondary

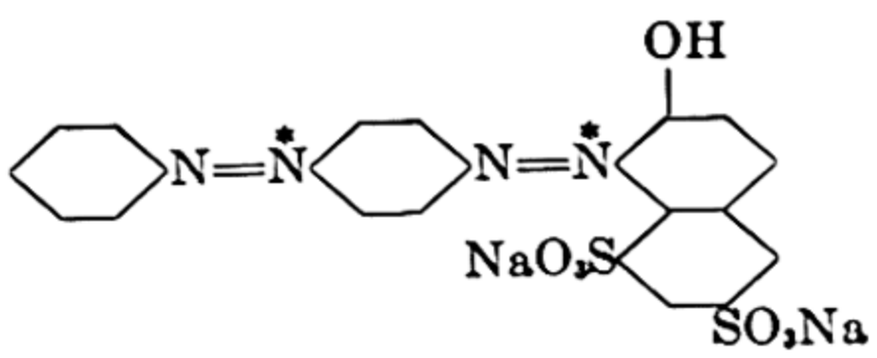
dis-azo dye. Primary dis-azo dyes are described later, under benzidine dyes. Several examples will be given.

Para-aminoazobenzene or "spirit yellow" is again the simplest case; it may be diazotized, and if then coupled with R acid, Cloth Red 2R is formed:

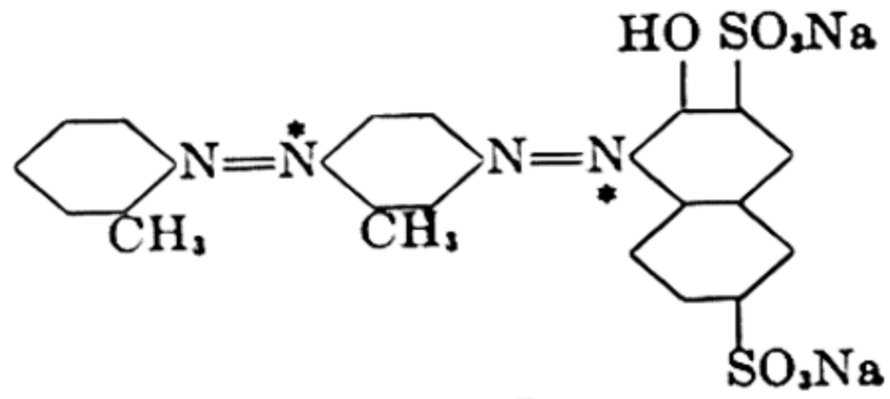


Diazotized para-aminoazobenzene *R acid* *Cloth Red 2R*

If the diazotized para-aminoazobenzene is coupled with G acid, Brilliant Crocein M results. Amino-azotoluene may be diazotized; and if this is coupled (alkaline) with R acid, Cloth Red B is obtained.

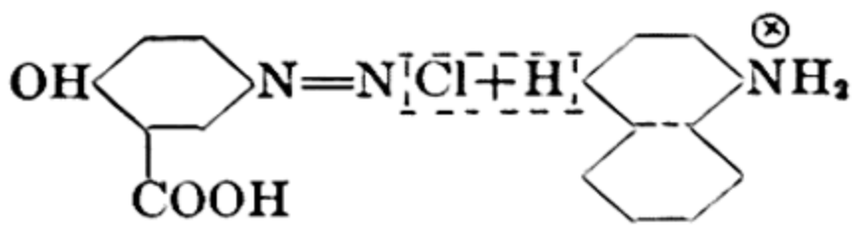


Brilliant Crocein M



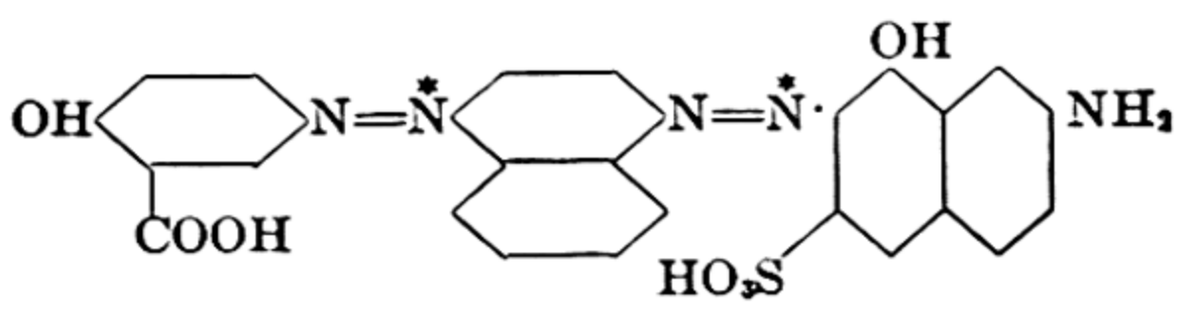
Cloth Red B

In the manufacture of Fast Black L, para-aminosalicylic acid is diazotized and coupled with α-naphthyl amine



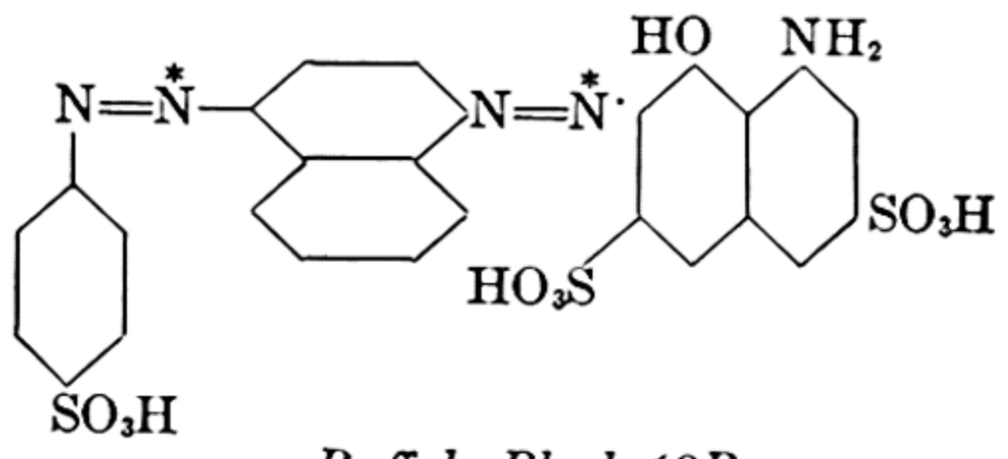
para-aminosalicylic acid (diazotized) and *α-naphthylamine*

This first dye, treated with sodium nitrite and acid, gives the diazotized product (the new azo group forms at ⊗) the solution of which is poured into the alkaline solution of γ-acid, forming Fast Black L.

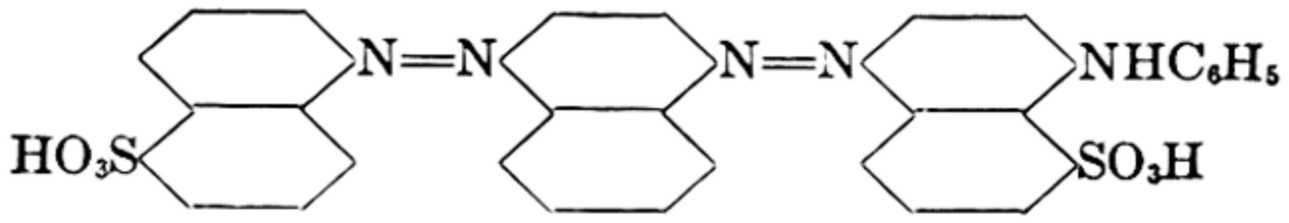


Fast Black L

Sufanilic acid diazotized and coupled with α-naphthylamine gives a mono-azo product which has a free amino group; this may be diazotized in turn and if coupled with 1-amino-8-naphthol-3: 6-disulfonic acid (H acid), the black dye called Buffalo Black 10B results. Another black in this class is Durol Black.

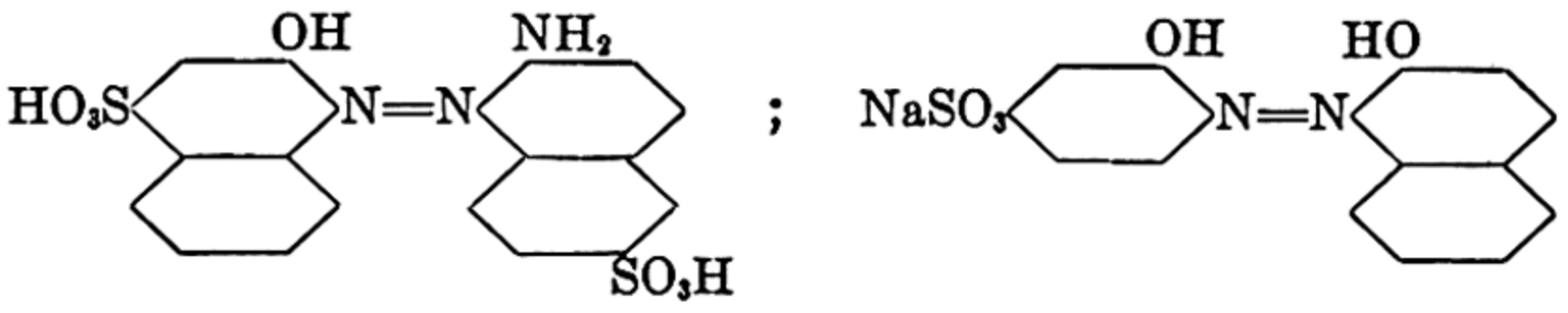


Buffalo Black 10B

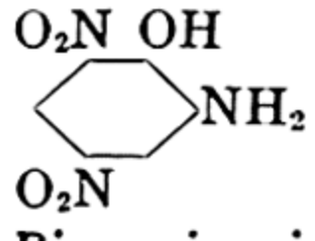


Durol Black

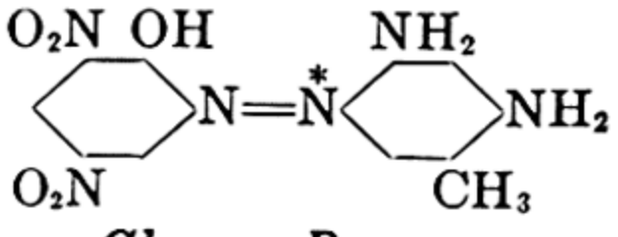
Mordant Azo Dyes. Certain azo dyes have the property of forming insoluble "lakes" with metallic oxides, which enhances the fastness properties. The metallic oxides are not introduced as such, but in the form of soluble salts, which are then made to form the corresponding hydroxide. In chroming, for example, sodium dichromate may be used; in coppering, copper sulfate serves. A good mordant dye should have a hydroxyl group or carboxyl ortho to each of the nitrogens in the azo group. Morever, valuable chrome dyes are derived by coupling diazotized ortho aminophenols (or naphthols) into various naphthols and β-naphthylamine derivatives. Examples:



Another example is Chrome Brown, made by diazotizing picramic acid and coupling it (acid) with *m*-toluenediamine:

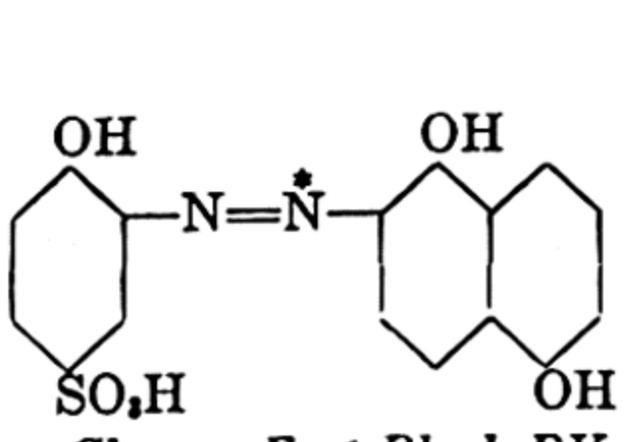


Picramic acid

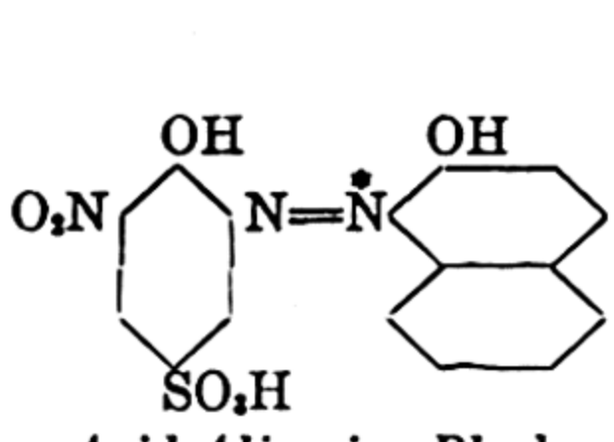


Chrome Brown

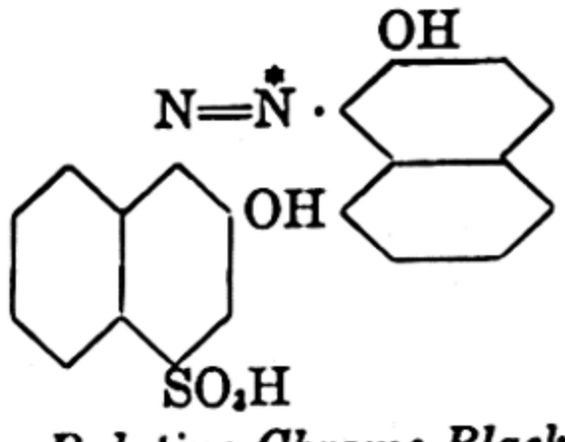
Still another example is Chrome Black PV, shown below; it is made by diazotizing ortho-aminophenol-para-sulfonic acid and coupling it (alkaline) with 1,5-dioxynaphthalene. Two other important members of this group are Acid Alizarine Black and Palatine Chrome Black, whose component parts are sufficiently shown in the formulas:



Chrome Fast Black PV

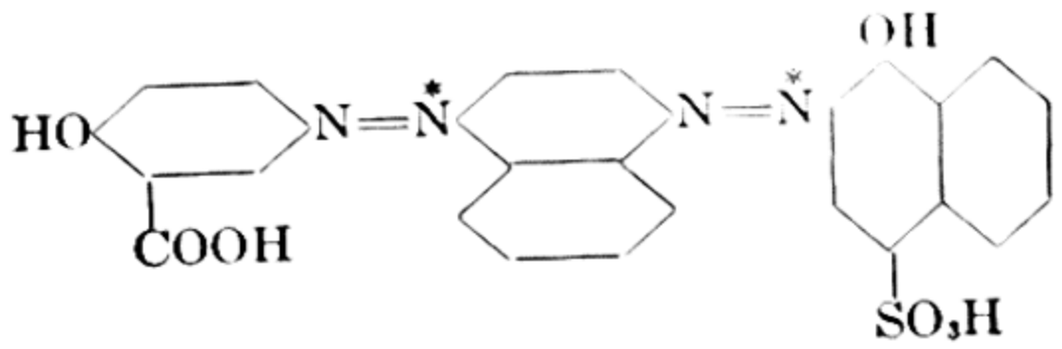


Acid Alizarine Black



Palatine Chrome Black

Diamond Black F is a secondary dis-azo dye which is also a mordant azo dye; it contains salicylic acid, α-naphthylamine, and Nevile and Winther's acid.

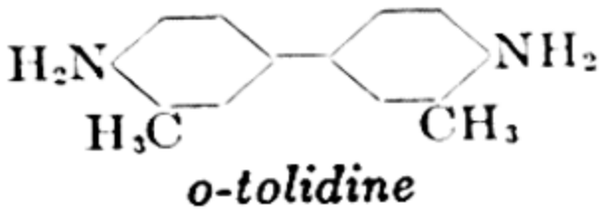


Diamond Black F

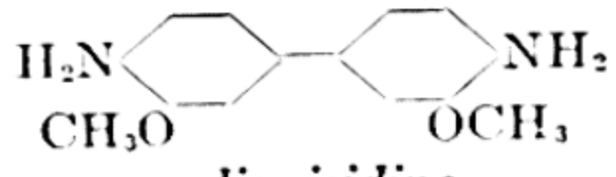
It will be noted that this dye has two lake-forming groupings.

Primary Dis-Azo Dyes. The azo dyes described in the previous divisions are mainly acid dyes for wool, or in the last division, mordant dyes for wool. Most of the primary dis-azo dyes in the present division are direct dyes for cotton, to which they are applied in the form of their sodium salt, which is also the form in which they are manufactured and shipped. Such dyes are dis-azo, since they contain two azo groups; and they are called primary, because the substance forming the starting point contains two primary amine (NH_2) groups; both may be diazotized, and both resulting diazonium groups may be coupled to some intermediate. Benzidine or a closely related substance is used for these dyes.

benzidine



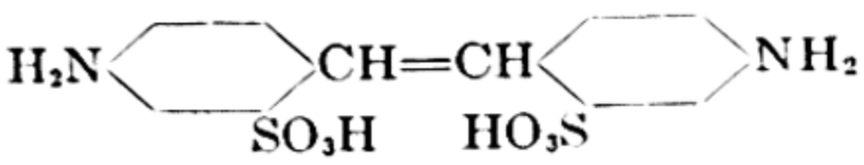
o-tolidine



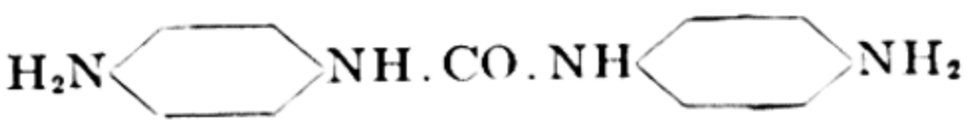
dianisidine

In addition to the primary dis-azo dyes there are tris-azo and tetrakis-azo dyes, which are direct dyes for cotton; furthermore there are dyes which have more than four azo groups.

Both amino groups in benzidine may be diazotized simultaneously without being even partly destroyed by the nitrous acid, and without needing to be protected by acetylation. This property is shared by other substances, among which diaminostilbene-disulfonic acid and diaminodiphenylurea derivatives are of importance.[8] The simultaneous diazotization of two amino groups is called tetrazotization, and the resulting product a tetrazo compound.[9]



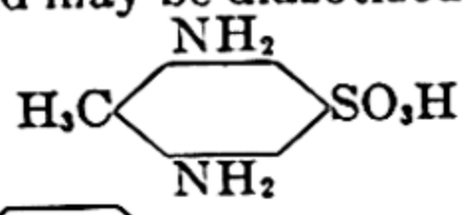
diaminostilbene disulfonic acid



diaminodiphenylurea

Benzidine in the free state is a white powder insoluble in water but soluble in dilute hydrochloric acid; both amino groups are diazotized

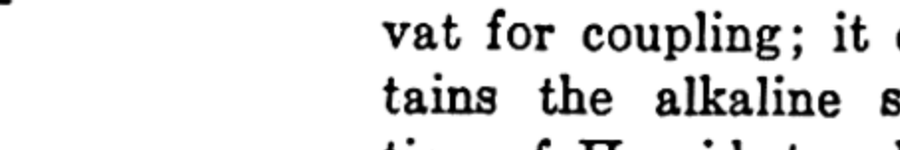
[8] Toluenediaminepara-sulfonic acid may be diazotized at both groups without protecting.



[9] Para-phenylenediamine $H_2N \cdot C_6H_4 \cdot NH_2$ cannot be diazotized at both groups without destruction.

together, and the resulting solution poured into the alkaline intermediate; if the same intermediate is to be introduced at each azo group, two mols [10] are used. The commercial procedure may be illustrated for Direct Blue 2B, which is made by coupling benzidine with two molecules of H acid.

benzidine



tetrazotized benzidine

Benzidine is suspended in water in a wooden vat equipped with an agitator (Fig. 223); five mols [10] of hydrochloric acid are added, and the whole brought to a boil by passing in live steam. The required amount of acid is four mols,

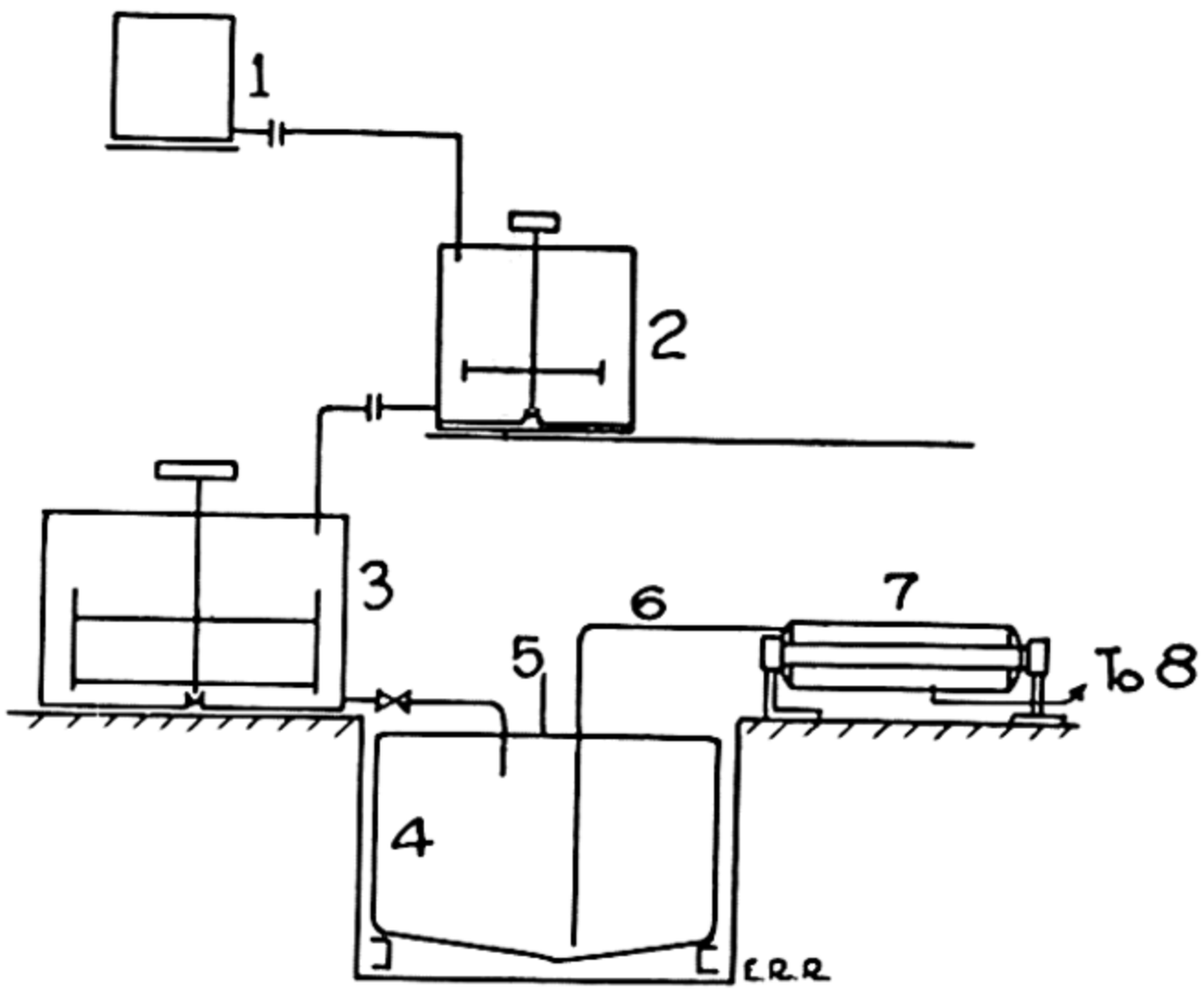


FIGURE 223.—Apparatus for manufacturing a benzidine dye; 1, sodium nitrite solution; 2, vat for tetrazotizing the benzidine hydrochloride; 3, vat for coupling; it contains the alkaline solution of H acid, to which contents of 2 are added; 4, blow-case; 5, compressed air; 6, discharge line to press; 7, press; 8, vacuum drier.

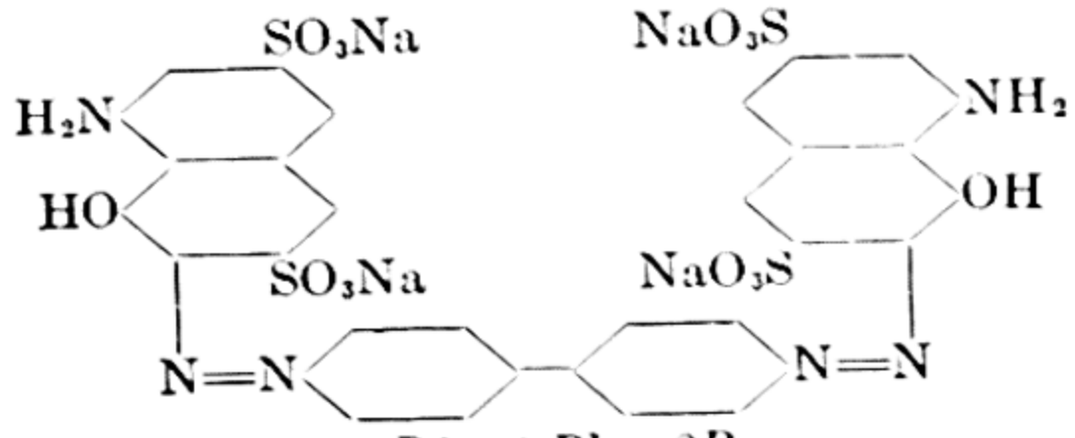
as indicated by the diazotizing reaction in the introduction to this chapter, two mols for each amino group; one mol is then the excess used. As soon as solution has taken place, ice is added, and a large part of the benzidine hydrochloride separates in a finely divided solid. Two mols of sodium nitrite, in solution in vat 1, are run in gradually; for 184 pounds of benzidine (one mol) the addition of 138 pounds of nitrite (two mols) would require two hours. In the meantime 446 pounds (two mols) of H acid are dissolved in an excess of soda ash in water (vat 3); to this, the contents of 2 are added, while stirring. Enough ice is added to keep the temperature at 5° C. The dye separates out only in part; in order to separate it all, the contents of the vat are warmed by passing in steam through a movable pipe; solid salt is added and dissolved, and the contents are then cooled; all of the dye precipitates. The soda ash used with the H acid is sufficient to form the sodium salt of the dye.

The suspension is run into a wooden plate-and-frame filter press [11]; the filtrate is tested, and if exhausted, it is run to the sewer. The cake is not

[10] The mol is the number of grams or pounds numerically equal to the molecular weight.

[11] Chapter 42.

washed, but merely freed from most of the adhering mother liquor by blowing with compressed air, while still in the press; the portion of the liquor retained must be removed by drying. The moist cake is discharged onto shallow trays which are placed in a circulating air drier wherein the moisture is removed at moderate temperatures which vary from 50 to 120° C. Stationary vacuum driers and drum driers are also used. All dyes discussed in this chapter are solids, and are sold in the form of powders.

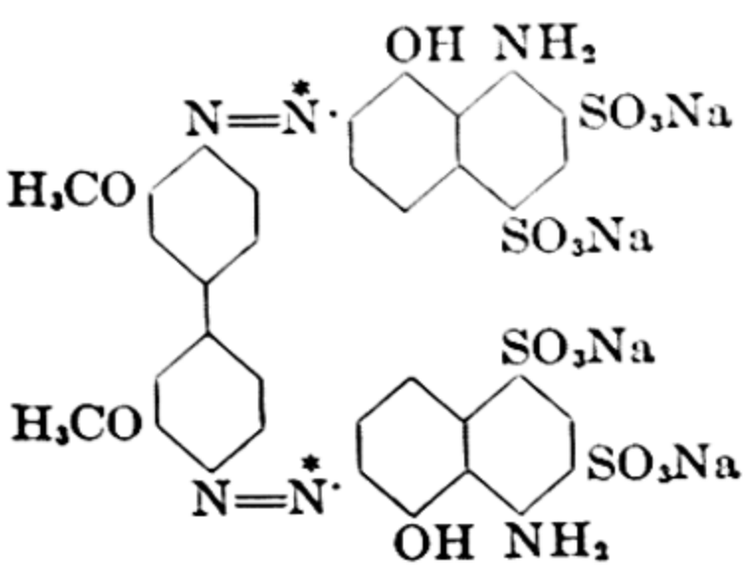


Direct Blue 2B

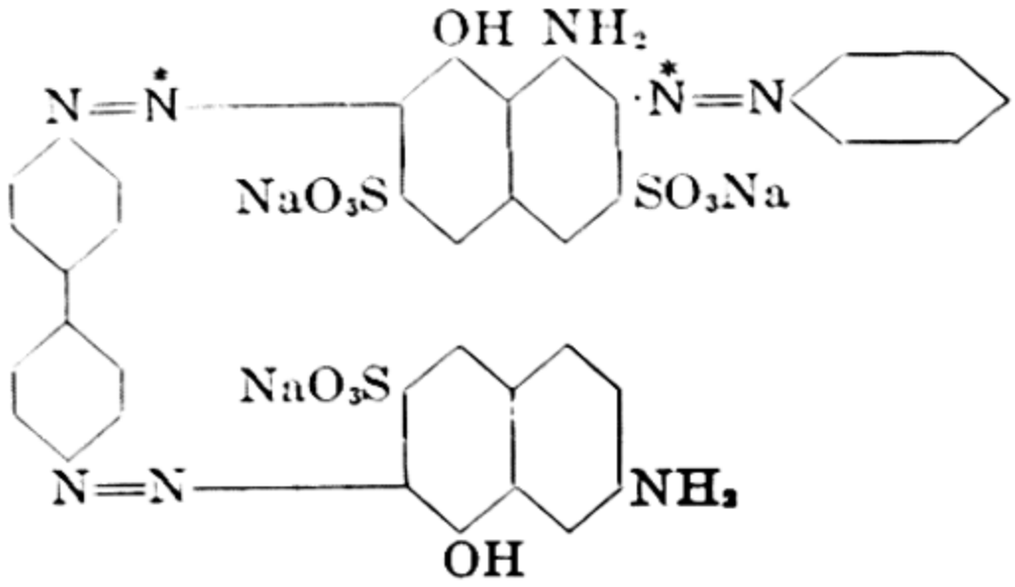
If it is desired to couple different intermediates at the two azo groups, it is possible to do so because one group couples fast while the other couples slowly. By pouring one mol of the intermediate into the tetrazonium solution, one of the diazonium groups is coupled in each molecule; the second remains free,[12] and may be coupled in a second operation. In such a case one vat for each intermediate must be provided, and must be placed at a higher level than the benzidine vat.

Direct Blue 3B is one shade bluer than the previous dye, and consists of tetrazotized tolidine coupled twice (alkaline) with H acid.

Sky Blue FF is dianisidine tetrazotized and coupled twice (alkaline) with SS acid,[13] Direct Blue N R contains tetrazotized benzidine coupled once (alkaline) with H acid, which has previously been coupled to diazotized aniline, and once with γ-acid (alkaline).



Sky Blue FF

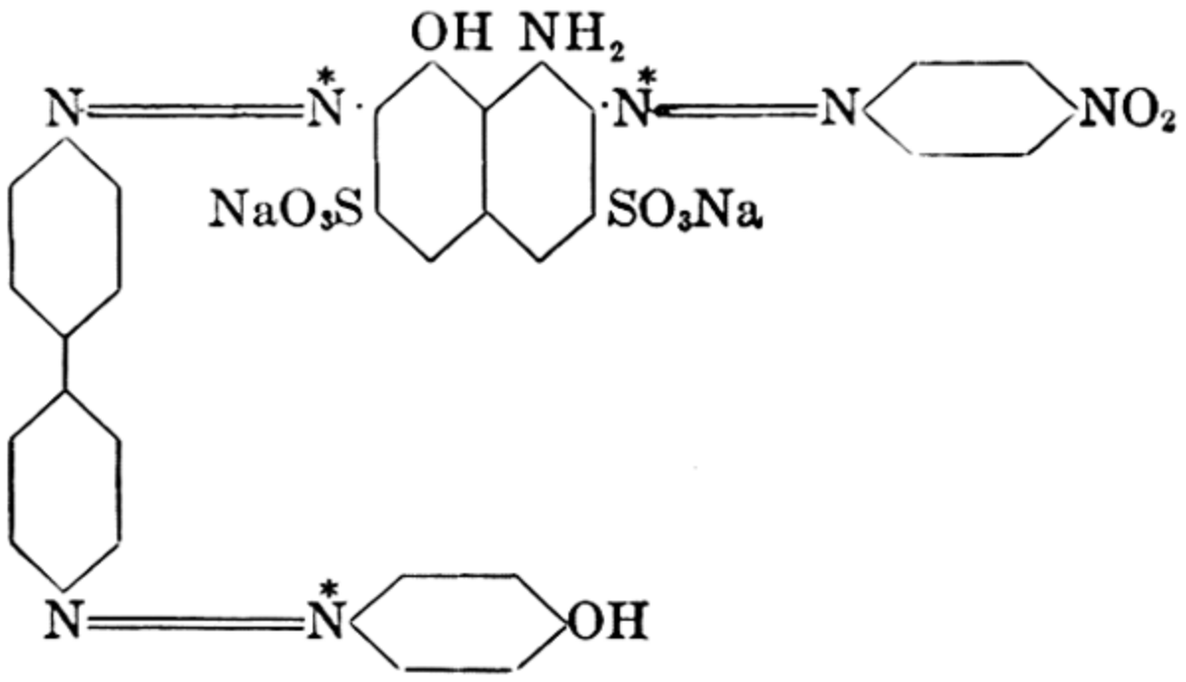


Direct Blue NR

A green dye is made by coupling tetrazotized benzidine with H acid (alkaline) which has previously been coupled (acid) with diazotized paranitraniline, and at the second diazonium group with phenol.

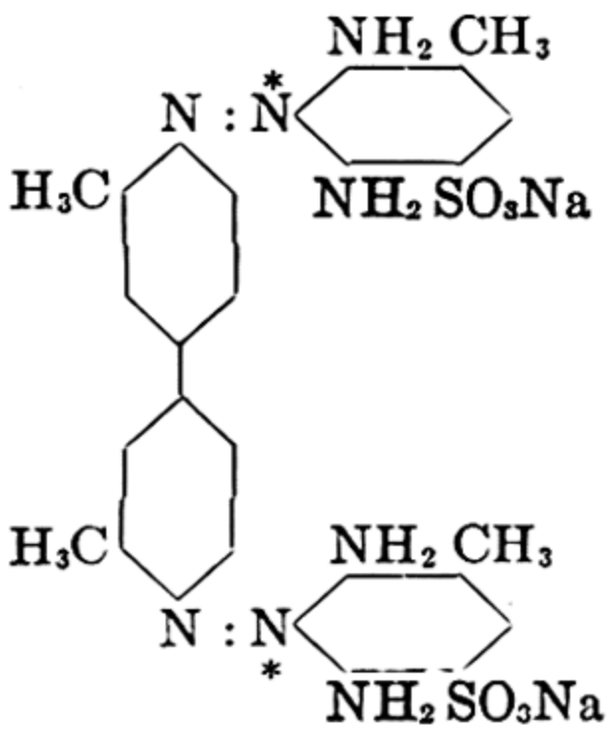
[12] The end-point for the first group is found by touching drops of the solution on a filter paper wetted with an alkaline solution of R acid. Absence of a red coloration indicates completion of coupling on one side.

[13] 1-amino 2-, 4-disulfonic 8-hydroxynaphthalene.

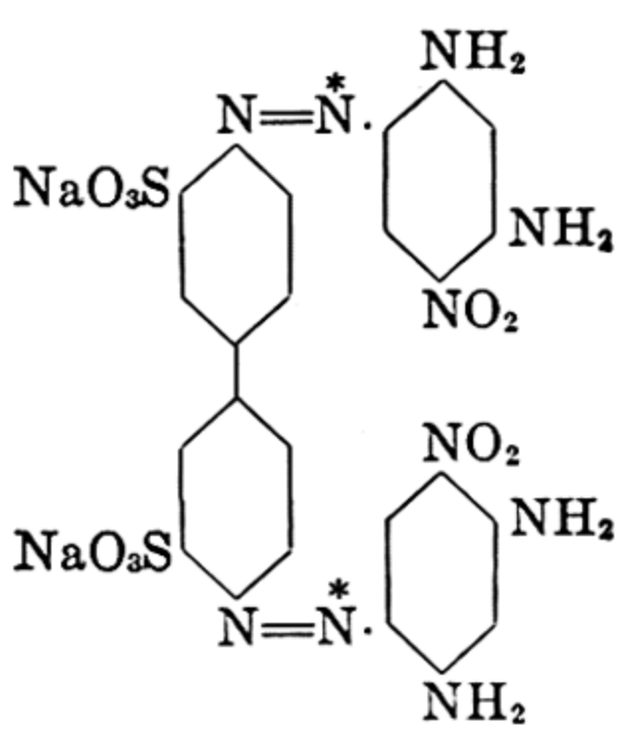


Direct Green

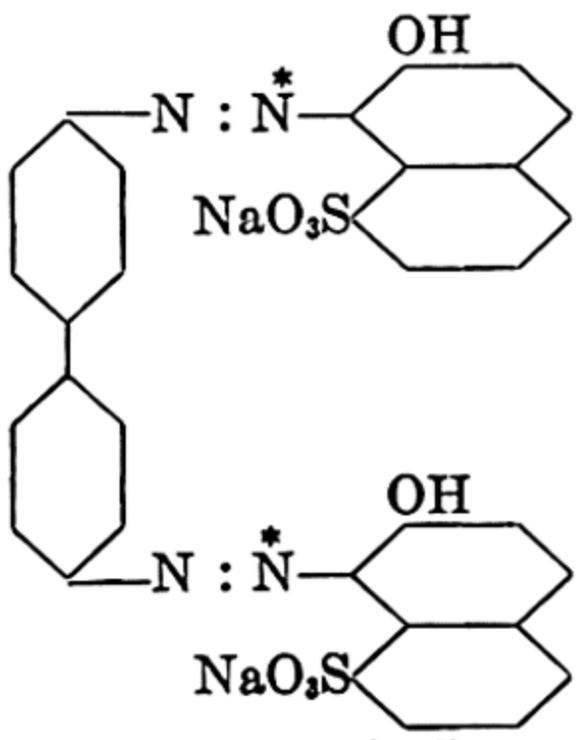
The composition of two orange dyes, two red dyes, a violet dye, and a black dye are exhibited by their formulas:



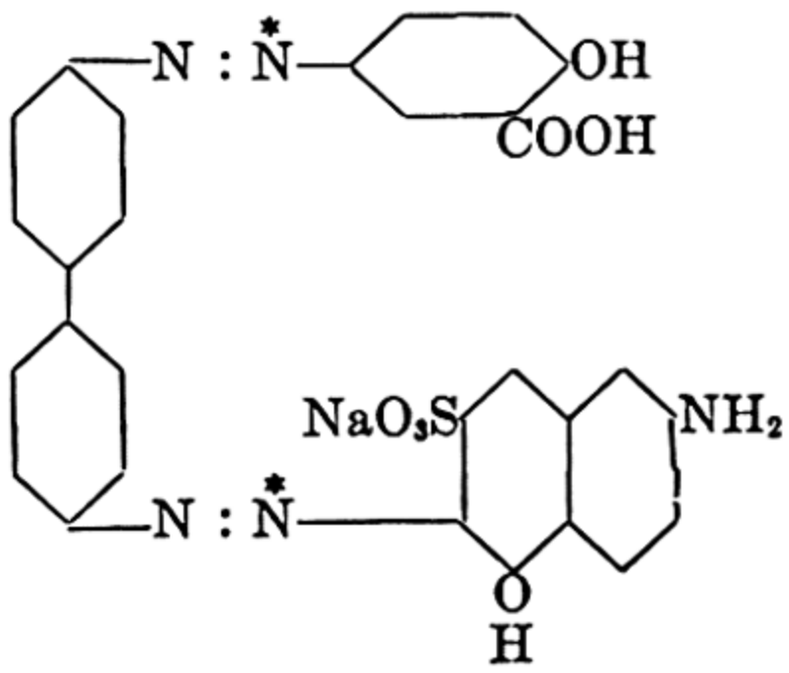
Toluylene Orange R



Pyramine Orange R

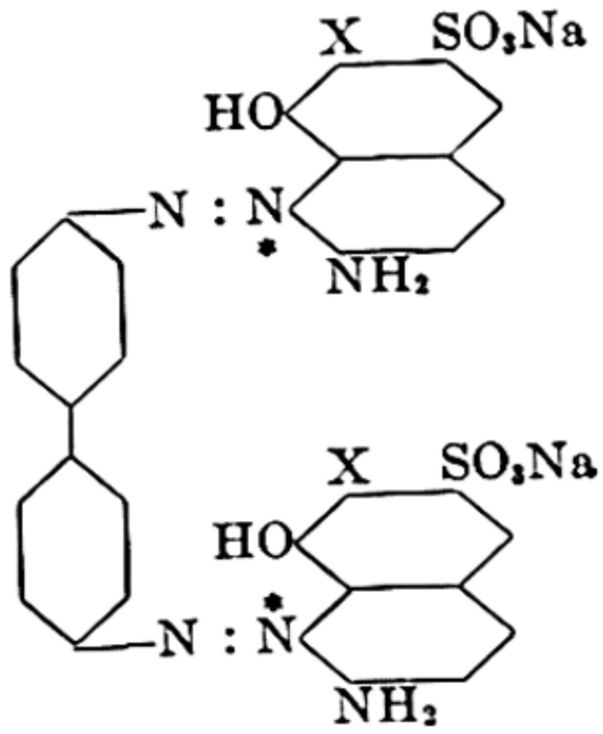


Bordeaux (red)

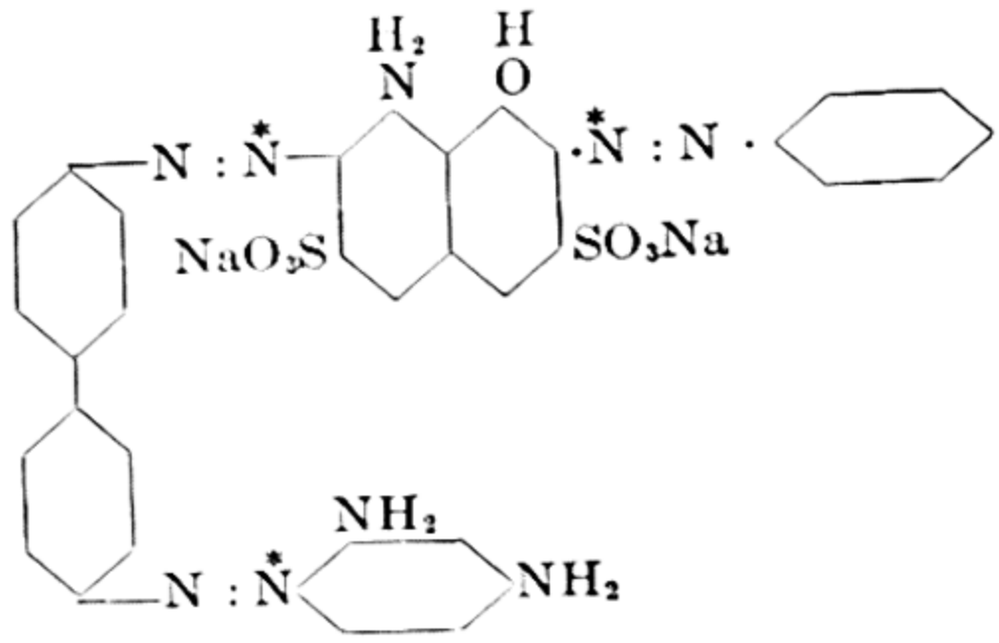


Direct Red J

In Direct Violet, the γ-acid is coupled acid, as the place of entry of the azo groups indicates; the coupling may be performed alkaline, when the place of entry will be adjacent to the hydroxyl group (at X X), and this slight difference in structure causes a blue dye to be produced, instead of a violet.



Direct Violet

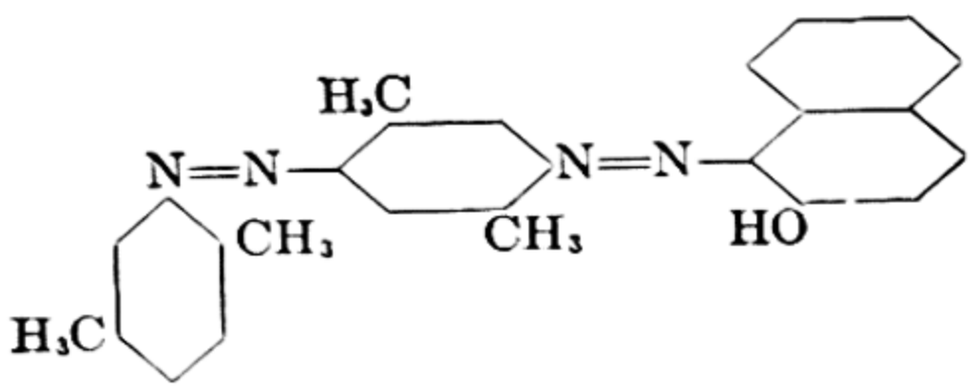


Direct Black

Stable Diazo Salts. A development is the manufacture of stable diazo salts, which consist of the uncoupled diazonium compounds in the form of its zinc salts. After forming the salt, the salted-out material is filtered and dried in a vacuum drier. The stable diazo salt is mixed with various anhydrous salts, such as magnesium sulfate and aluminum sulfate. The dry diazo salt is shipped to the customer, who places it in water solution, and passes cotton skeins or cloth through it. The goods are wrung out, and sent through an alkaline Naphthol AS derivative (or a Naphthol AS-G [14] derivative) bath, so that coupling takes place on the cloth. The result is a light-fast dye. It will be noted that the process resembles vat dyeing; it requires much simpler formulas, fewer chemicals, less skill, and less time.

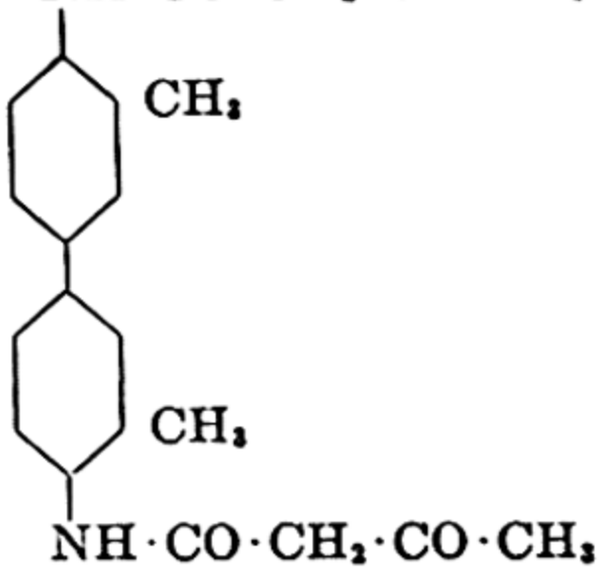
The diazo compound is stable by virtue of the formation of its salts; hence the name.

Dye for Gasoline. In order to color gasoline red, a dye called Oil Red EG is used, among others. Its formula will indicate that it is made by diazotizing aminoazoxylene, and coupling it with β-naphthol.



Oil Red EG

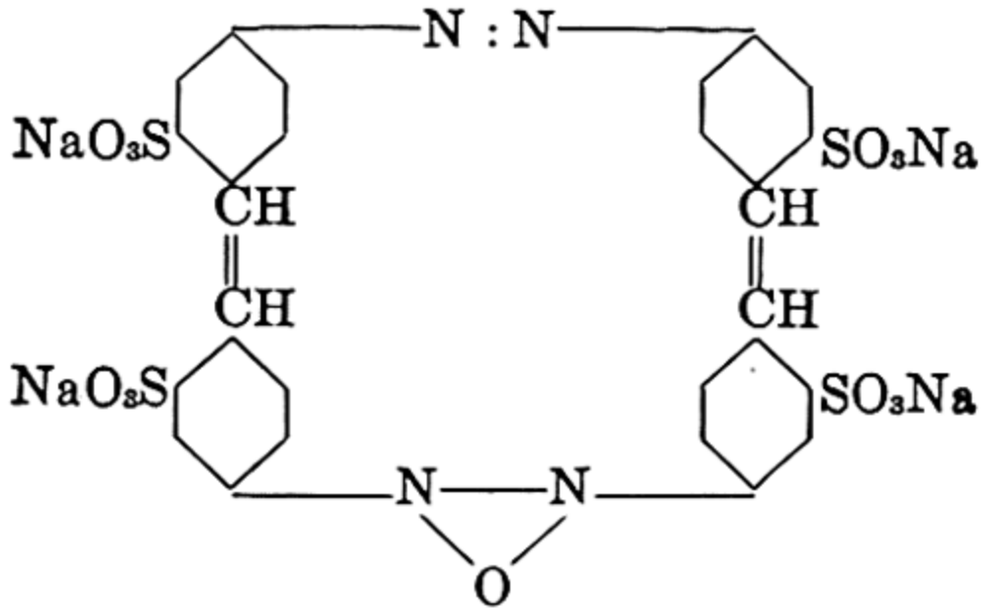
[14] For example



Stilbene Dyes

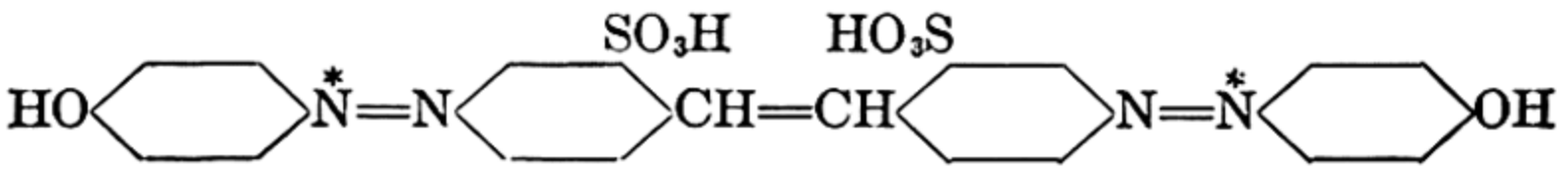
The stilbene dyes contain the chromophore —N:N—, usually not obtained however by diazotization of amines, but by the action of caustic soda on para-nitro-toluene sulfonic acid. The colors formed by this reaction vary with length of heating, temperature, and concentration of caustic, so that in order to duplicate a color, the exact conditions must be observed. Little is known of the constitution of such dyes, and most of the brands on the market consist of mixtures of products formed during the reaction.

The Mikado dyes belong to this group; Sun Yellow, shown below, is an example:



Sun Yellow

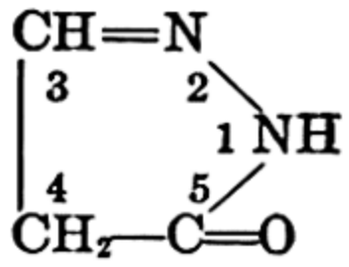
Another example of the stilbene dyes is Brilliant Yellow (used chiefly for tinting paper); its formula is given below. Treated with ethyl chloride (C_2H_5Cl) under pressure, the two hydroxyls are changed to the ether groups (OH becomes OC_2H_5), and the more important Chrysophenine, a bright yellow dye which is faster than Brilliant Yellow, is produced.



Brilliant Yellow

Pyrazolone Dyes

The pyrazolone dyes contain the pyrazolone[15] nucleus (usually in the form of the 1-phenyl pyrazolone or a derivative thereof.

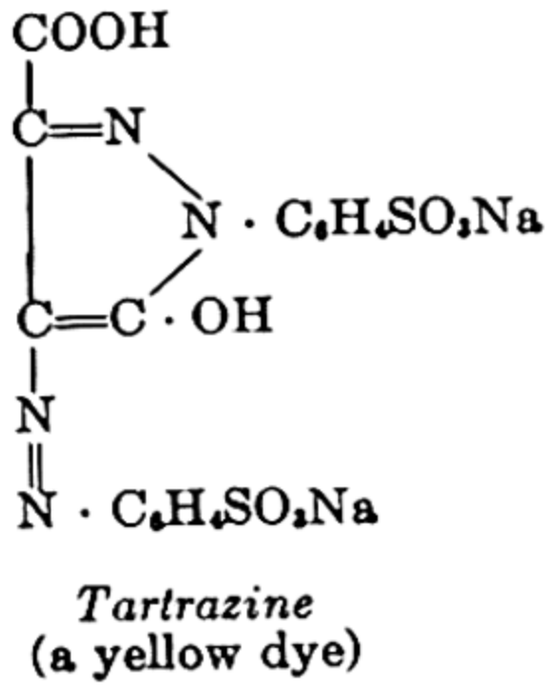


Tartrazine, a favorite yellow dye, will be the example for this group. It is made by mixing a solution of 1 mol dioxy-tartaric acid[16] and a solution of 2 mols phenylhydrazinesulfonic acid; on heating slowly, the dye forms.

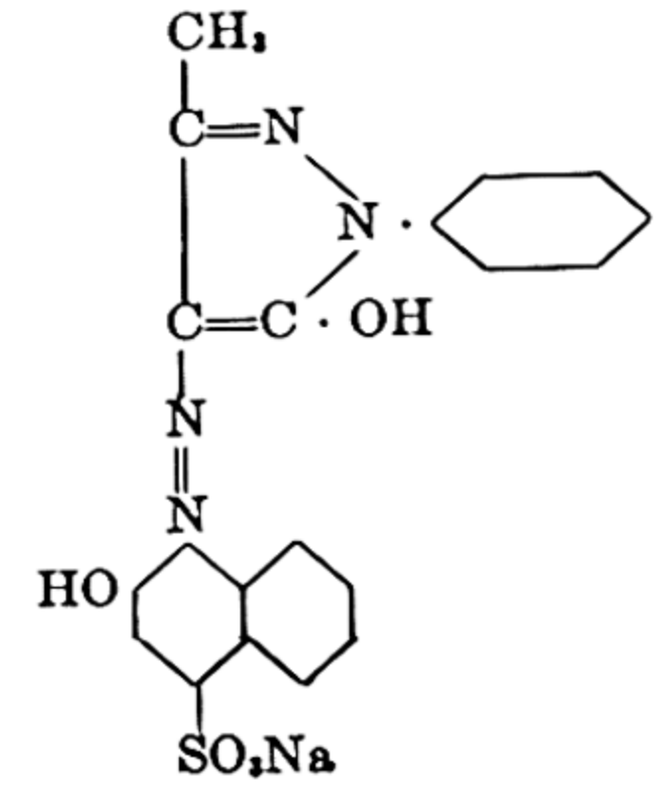
Pyrazolone derivatives made from ethyl aceto-acetate condensed with phenyl hydrazine, para-sulfonic phenyl hydrazine, 3,6-dichloro-4-sulfophenyl

[15] 1-phenyl-2,3 dimethylpyrazolone is antipyrine, a pharmaceutical.
[16] Made by oxidizing tartaric acid with nitric acid.

hydrazine, and others, coupled with diazonium compounds of the benzene series, yield light-fast, clear yellows for wool. Coupled with a diazonium compound of the naphthalene series, a chrome red is formed; coupling takes place at 4.



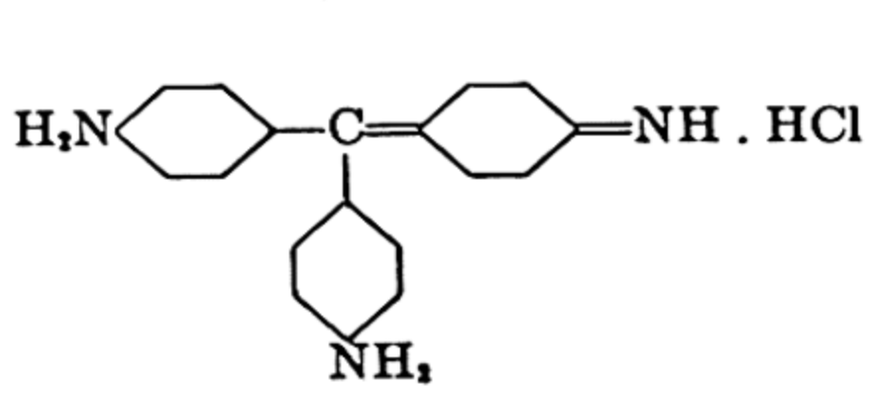
Tartrazine
(a yellow dye)



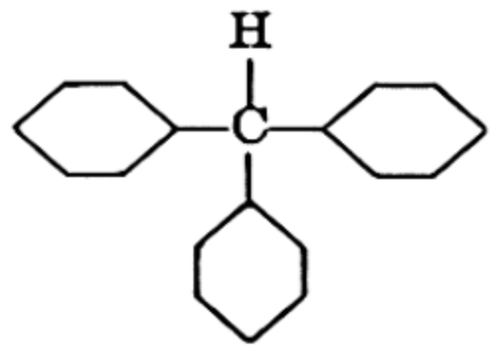
Eriochrome Red B

Triphenylmethane Dyes

Rosaniline, fuchsine, malachite green, and crystal violet are members of this class; its chromogen has three benzene nuclei attached to a central carbon, the so-called methane carbon, but one of the benzene structures has been altered to the quinone structure. The triphenylmethane dyes may be either basic or acid dyes. The salt-forming groups in basic dyes are usually in the para position and are amines or substituted amines. The salt-forming groups in the acid dyes can be sulfonic acids, carboxylic acid or phenol derivatives, that is a substitution for the hydrogen in the hydroxyl. These groups (except in the case of the hydroxyl) are seldom in the para position, and are often not in the three benzene rings forming the triphenylmethane nucleus. Para-fuchsine, or Fuchsine, is the simplest triphenylmethane dye; it is a hydrochloride; the chromogen is shown next to it.

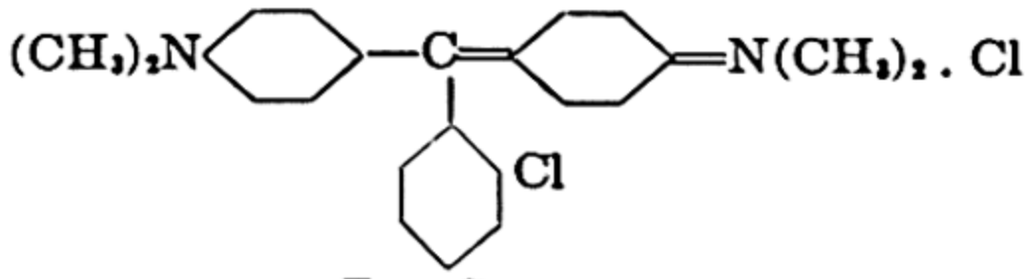


Fuchsine
(red)



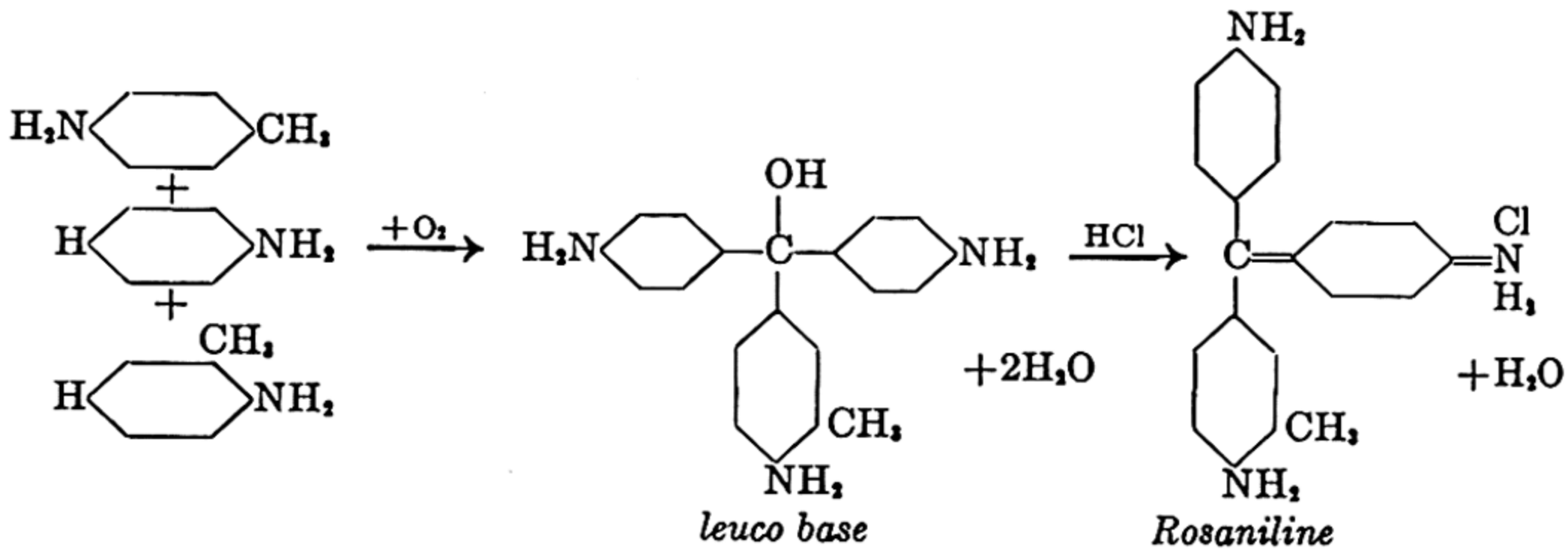
Chromogen

Fuchsine is the salt of a weak base; it is easily changed by alkali to the colorless carbinol. If chlorine is present in the molecule, ortho to the methane carbon, the new dye is somewhat more alkali-resisting. As example, Fast Green is given as:



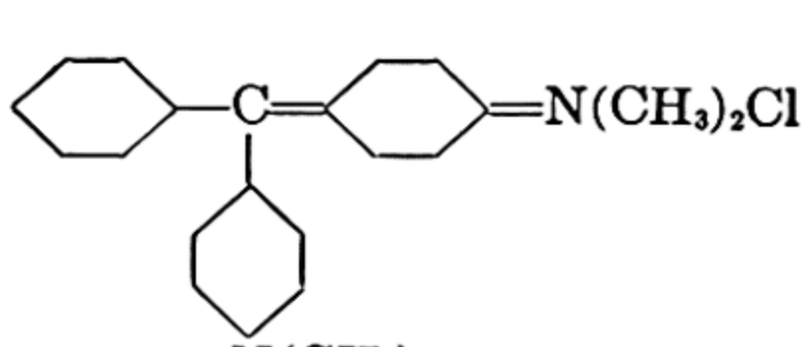
Fast Green

One of the methods of manufacture may be illustrated by Rosaniline, which is made by condensing 1 mol each of aniline, paratoluidine and ortho-toluidine in the presence of nitrobenzene as oxidizer. On neutralizing the resulting carbinol with hydrochloric acid, the dye forms.



leuco base *Rosaniline*

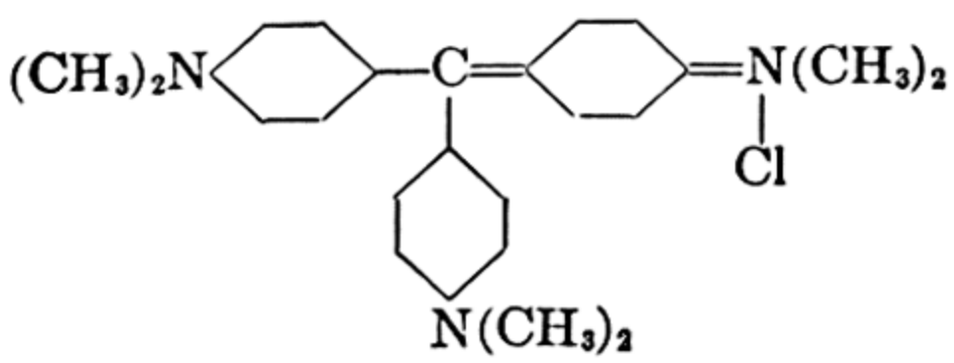
A second method is the condensation of aromatic aldehydes, such as benzaldehyde, $C_6H_5 \cdot CHO$, or monochlorobenzaldehyde, $Cl \cdot C_6H_4 \cdot CHO$ with aromatic amines. Benzaldehyde (1 mol) condenses with 2 mols dimethylaniline to form a leuco base which, on oxidation with lead peroxide and treatment with hydrochloric acid, yields Malachite Green.



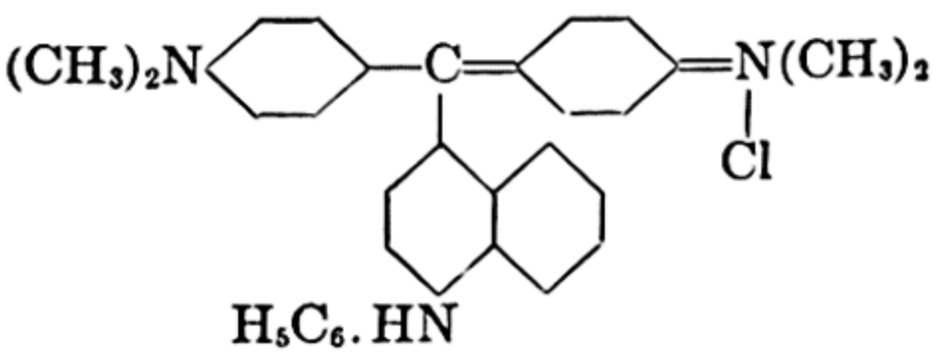
Malachite Green

The condensation of ortho-chlorobenzaldehyde with dimethylaniline leads to Fast Green, with the formula as given above.

Ketone condensations, a third method of manufacture, are quite different in that such condensations are made in organic solvents or diluents using phosphorus oxychloride. An example is the condensation of Michler's ketone $(CH_3)_2N \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot N(CH_3)_2$ [made by passing phosgene ($COCl_2$) into dimethylaniline ($C_6H_5 \cdot N(CH_3)_2$] with aromatic bases, such as dimethylaniline itself; there is formed a carbinol which is changed by hydrochloric acid to Crystal Violet. The same ketone condensed with a substituted α-naphthylamine gives Victoria Blue.

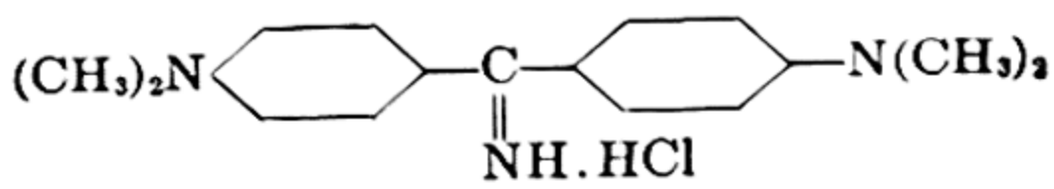


Crystal Violet



Victoria Blue

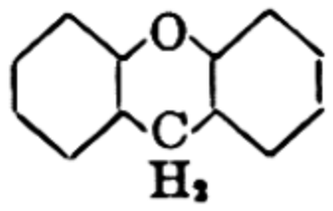
The diphenylmethane dyes are unimportant, except for Auramine, a yellow dye.



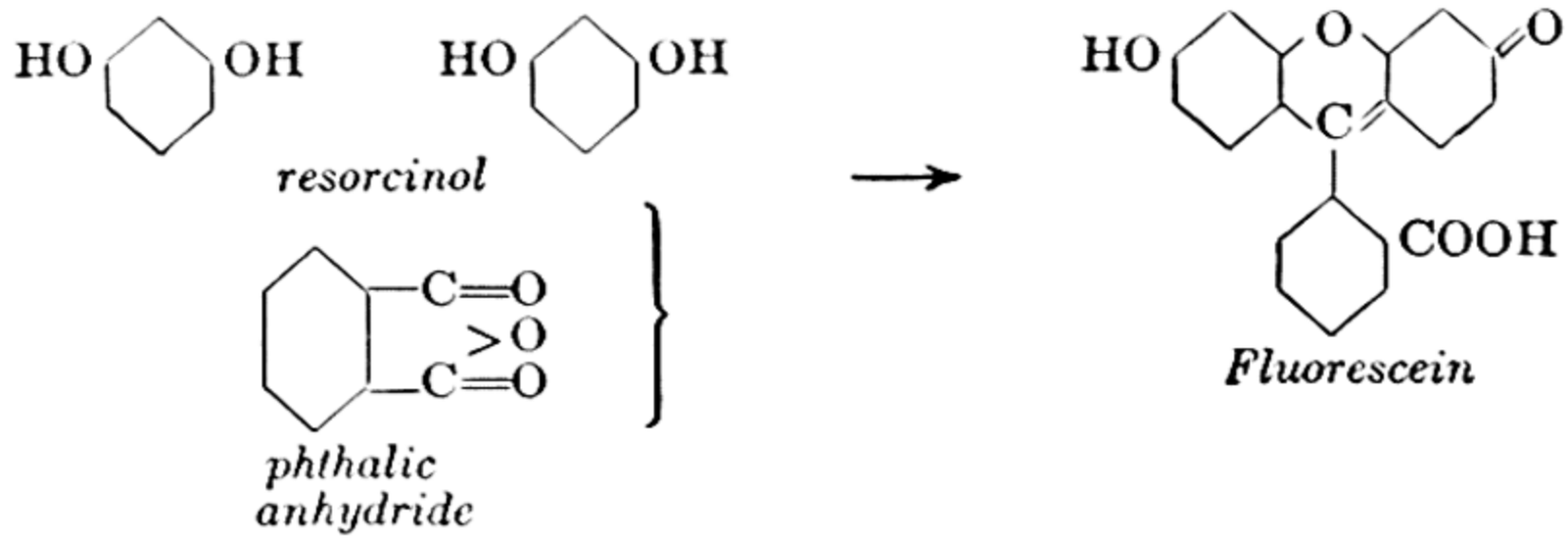
Auramine

Xanthene Dyes

Fluorescein, eosine, and rhodamine represent each a series of dyes which contain the same central structure, called xanthene, with the formula



they are therefore classed together as xanthene dyes. Fluorescein is made by heating in an iron vessel phthalic anhydride (1 mol) and resorcinol (2 mols); the temperature is regulated by means of an oil or metal bath and kept at 220° C. for 7 hours. The melt is dissolved in caustic soda, and the fluorescein precipitated by acidifying; it is a yellow-red powder. Its alkaline solution fluoresces green-yellow. Fluorescein in the form of its sodium salt is called Uranine, and is widely used to trace underground flow of water.

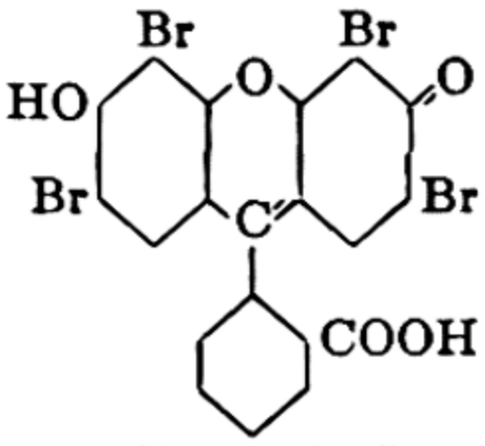


resorcinol

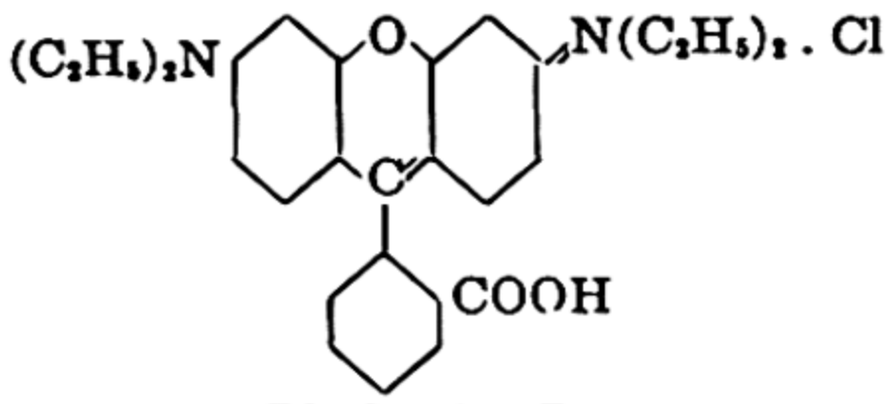
phthalic anhydride

Fluorescein

Dissolved in alcohol and treated with bromine while warm, four equivalents are absorbed to form tetrabromofluorescein or eosine.



Eosine (red)



Rhodamine B

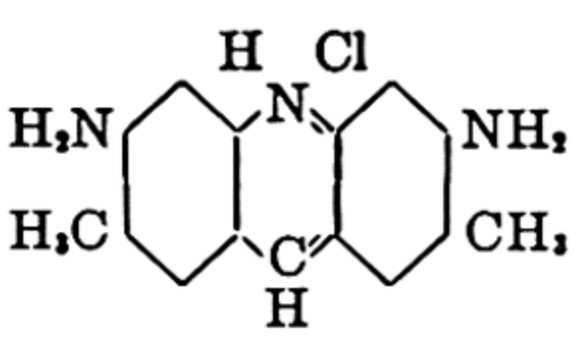
A number of other eosines are obtained by making dinitrodibromofluorescein, and similar compounds, or their esters.

Erythrosine is a tetraiodofluorescein; Phloxine the tetrabromdi-chlorofluorescein.

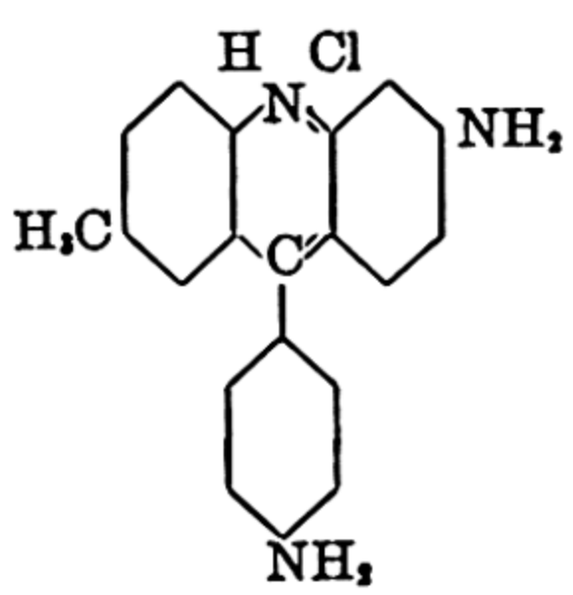
Rhodamines are made by condensing phthalic anhydride with ethylated meta-aminophenols and treating with hydrochloric acid. Rhodamine B, a bluish-red dye, is shown above.

Galleine is a good mordant dye for cotton; it is made by condensing phthalic anhydride (1 mol) with pyrogallol, 1,2,3-trihydroxybenzene, (2 mols).

Related to the xanthene dyes are the acridines, azines, oxazines and thiazines. Acridine Yellow results from the fusion of meta- tolylene-diamine with glycerine and oxalic acid followed by oxidation with ferric chloride. Phosphine is a by-product of the manufacture of Fuchsine, and is an acridine dye.

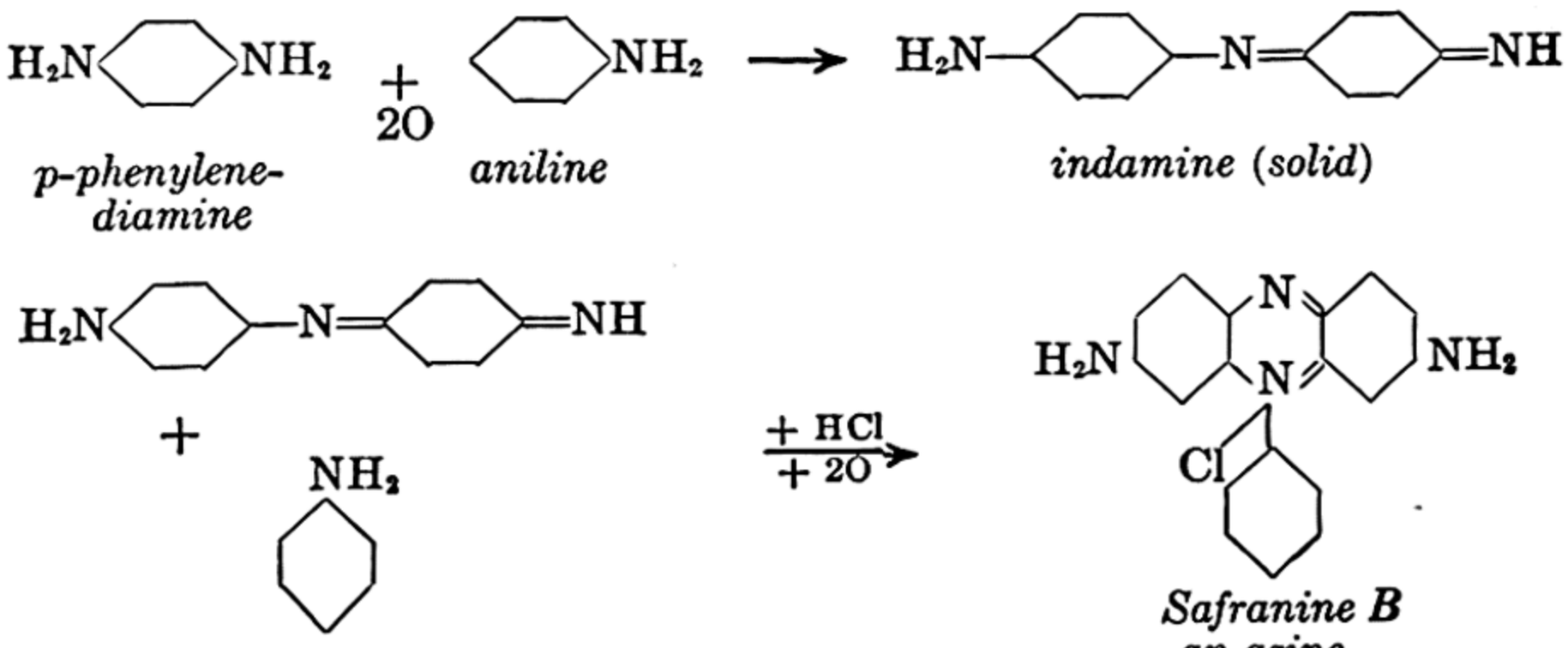


Acridine Yellow



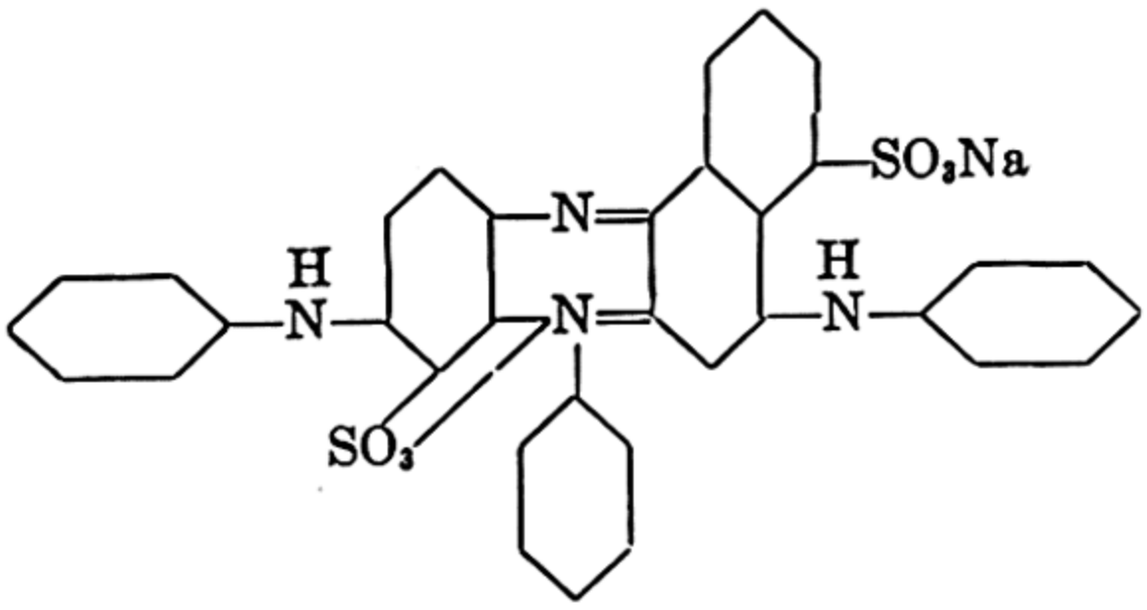
Phosphine

The quinone-imide dyes are derivatives of indamine and indophenols. Dyes of the indamine type are now used extensively in color photography. All the color films on the market today are made of dyes of this type, actually formed during development of the films. The quinone-imide dyes are important also because azine dyes are made from them. Indamine is made from para-phenylenediamine and aniline; Safranine B, an azine dye, is made as shown below. The azine nucleus has two nitrogen atoms in the central ring.

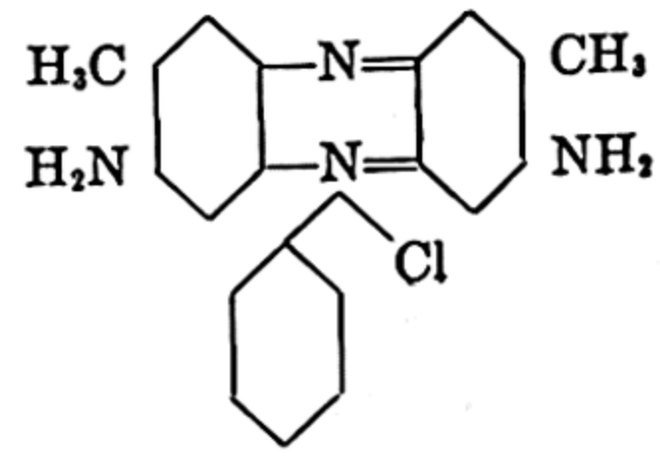


p-phenylene-diamine + *aniline* → *indamine (solid)*

Safranine B
an azine

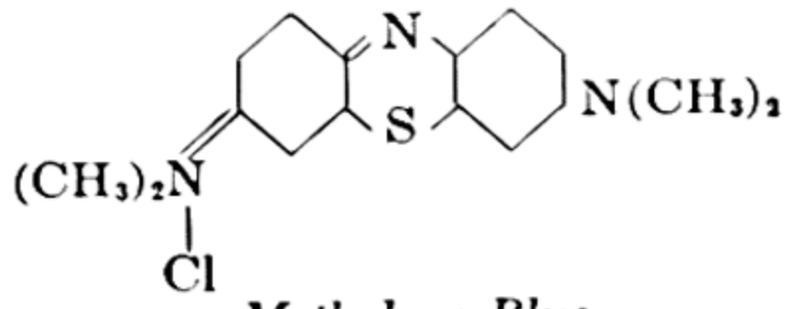


Wool Fast Blue BL



Safranine

Methylene Blue is a thiazine; its nucleus contains nitrogen and sulfur in its central part:



Methylene Blue

On nitrating Methylene Blue, Methylene Green is formed. Meldola's Blue is an oxazine dye.

Alizarine Dyes

The alizarine dyes may be considered derivatives of anthraquinone; they are actually made from anthraquinone in many cases, but some of them (for example, Alizarine Brown) are made by condensing two benzene derivatives. Anthraquinone is the chromogen which contains two chromophoric groups, the two quinonoid $>C=0$ groups.

Alizarine dyes may be broadly divided into two classes: (a) alizarine mordant dyes and (b) acid alizarine dyes. The former are applied to the fiber with the aid of mordants, usually salts of aluminum, calcium or chromium, while for the latter an aqueous solution of the dye in the presence of a mineral acid is used.

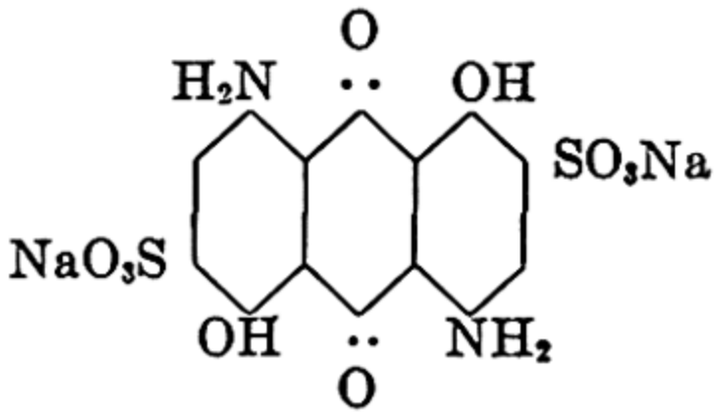
Alizarine Mordant Dyes: These dyes must contain groups such as OH or COOH which will combine with the metal in the mordant. With two OH groups at 1 and 2 (consult Chapter 27 for the numbering) the dye is alizarine proper which, when applied to wool with an aluminum mordant, gives the well known Turkey Red, and when converted to its calcium salt forms a bluish red powder much used in pigment work. Whereas alizarine is very sparingly soluble in water, if sulfonic groups are introduced, the resulting dye is quite soluble in water (Alizarine Red S.) By introducing additional hydroxy, nitro or arylamino groups into the alizarine molecule, a large number of other mordant dyes of various shades can be obtained (formulas in Chapter 27).

Alizarine is made by heating under pressure 100 parts of silver salt (this is the sodium salt of anthraquinone 2-sulfonic acid, so called because of its silvery crystals), 250-300 parts of caustic soda, 10 to 15 parts of potassium chlorate, and some water, to 180° C. in a steel autoclave provided with an agitator. The operation is an alkaline fusion, discussed in the previous chapter, but the hydroxyl groups introduced number one more than the sulfonic group present. The resulting melt is blown into water, acidified to decompose the sodium alizarate, and the precipitated alizarine filtered, washed and standardized to a 20 per cent paste.

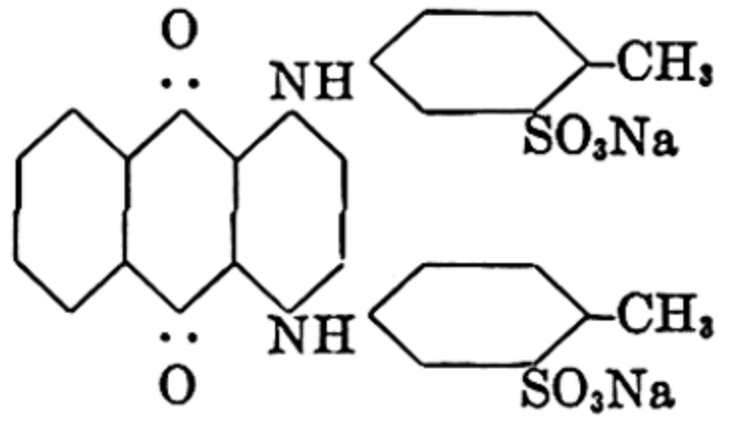
Alizarine Orange is 3-nitro alizarine. Other dyes of this class are Alizarine Brown (1,2,3-trioxy anthraquinone), Alizarine (Yellow Shade) (1,2,6-trioxy anthraquinone), Alizarine Bordeaux (1,2,5,8-tetraoxy anthraquinone), Alizarine Blue 2RC (1,2,4,5,6,8-hexoxy anthraquinone). The most important water-soluble dyestuff of this class is Alizarine Blue Black B, ob-

tained by condensing aniline with 1,2,4-trioxy anthraquinone (Purpurin), and sulfonating the resulting base. It is applied to wool with a chrome mordant and is exceptionally fast to light and washing.

Acid Alizarine Dyes: These dyestuffs are derivatives of anthraquinone which as a rule contain amino or arylamino groups (*e.g.*, anilido, toluido) and are soluble in water by virtue of the sulfonic acid groups which have been introduced by sulfonation or the like. The two most important of these are:

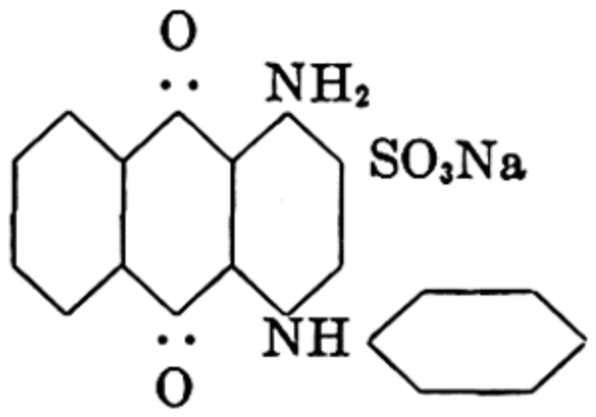


Alizarine Sapphire B



Alizarine Cyanine Green GEx

Of more recent origin are dyestuffs of which the simplest member is:



Alizarine Sapphire A

Vat Dyes

A vat dye is insoluble in water, dilute acid or alkali; it must be reduced to the so-called leuco compound in order to be soluble, and it is only in this state that it has affinity for the fiber. The reduction was formerly done in a vat, hence the name, vat dyes. The reduction is performed with sodium hydrosulfite $Na_2S_2O_4$,[17] a powerful reducer; sodium sulfide reduces only partly. After application to the fiber, the original insoluble material reforms on exposure to the air by oxidation.

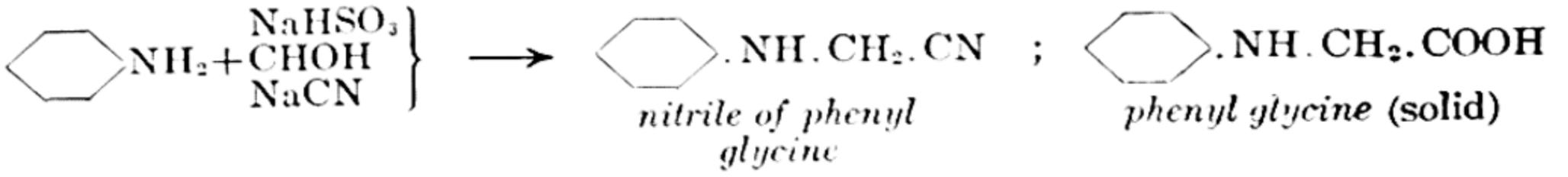
Vat dyes may be classified into three broad groups: (a) Indigoid and Thioindigoid; (b) Quinonoid; (c) Miscellaneous which do not fit in (a) or (b), such as Hydrone Blue.

The Indigoid Group: Artificial indigo was synthesized originally from anthranilic acid and chloroacetic acid, followed by several other operations; this procedure is now obsolete for indigo, but is still used for thio-indigo. The next procedure is simpler; aniline and chloroacetic give phenyl glycine, and this condenses to indoxyl by fusion with alkali.

The really modern method is remarkably simple; it is a combination of two reactions described in the patent literature. The first step is the preparation of phenyl glycine. In a water solution of sodium bisulfite, formaldehyde is placed; to this is added aniline oil, and then sodium cyanide. The

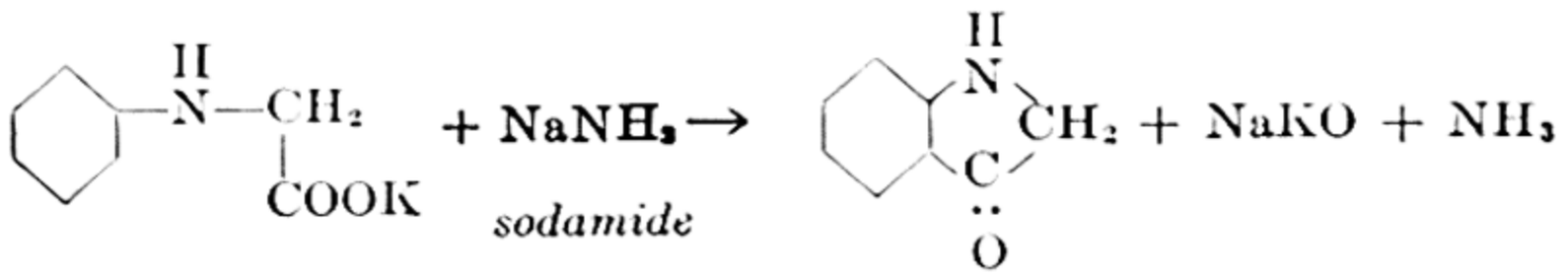
[17] Chapter 4.

nitrile is formed in the cold, separated by filtration and washed free from the sulfite salt. The nitrile crystals are warmed in an alkaline slurry; ammonia is evolved, and a solution of the phenyl glycine salt is formed.[18]



nitrile of phenyl glycine — *phenyl glycine* (solid)

In the second step, the phenyl glycine salt is condensed by heating with a eutectic mixture of potassium and sodium hydroxide,[19] in the presence of sodamide,[20] which removes the water formed. The yield is excellent, mainly because the reaction temperature, 200° to 220° C., is much lower than in previous methods. The higher temperatures meant greater decomposition of the indoxyl.



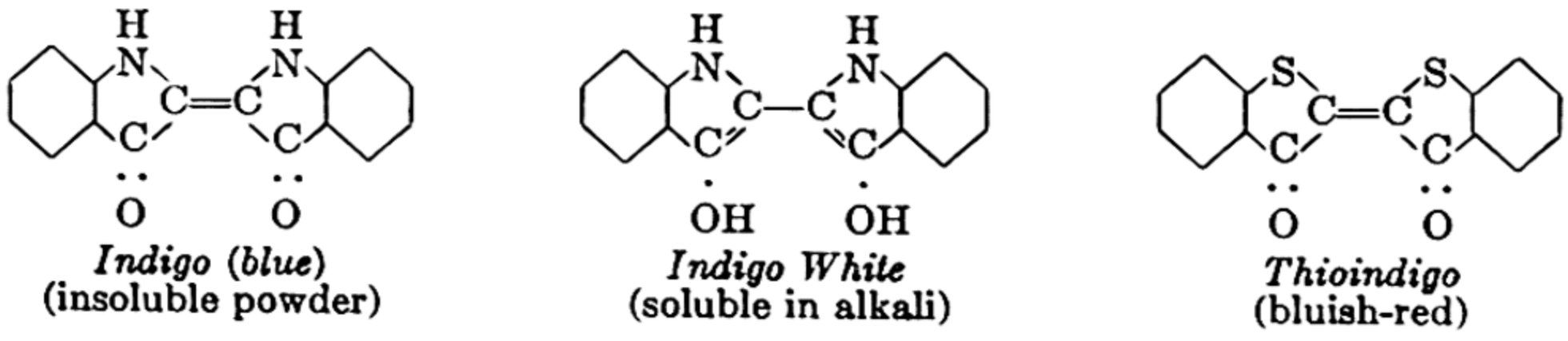
potassium salt of phenyl glycine — *indoxyl*

After the fusion, water is added, and in this alkaline solution, air is blown; the indoxyl is oxidized to indigo, which precipitates and is filtered off, washed, and dried. Two molecules of indoxyl form one of indigo with the removal of 4 hydrogen atoms (as water).

Continuous processes for the manufacture of indigo have been devised and installed in two German plants, at Hoechst (near Frankfort) and Ludwigshafen, both part of the I. G. Farbenindustrie.[21]

Hydroxyethylaniline, formed when ethylene chlorhydrin is treated with aniline, is synthesized commercially to indigo with a molten mixture of potassium and sodium hydroxides containing ground calcium oxide; hydrogen is evolved. The thioindigos are made from phenyl thioglycine derivatives.

In order to apply indigo to fibers, it is reduced to indigo white, which is soluble in alkalies.



Indigo (*blue*) (insoluble powder) — *Indigo White* (soluble in alkali) — *Thioindigo* (bluish-red)

[18] German Patent 135,332, also 151,538.

[19] German Patent 137,955.

[20] Sodamide is made by passing dry ammonia gas over melted sodium in a closed vessel, hydrogen is formed, and is burned at a suitable outlet. $2Na+2NH_3=2NaNH_2+H_2$. Sodamide is a white solid melting at 120° C. German Patent 117,623. These four patents are reproduced in Friedlaender's collection (*see* reading references).

[21] See "Continuous Processes for Indigo," J. G. Kern and Harry Stenerson, *Chem Eng. News*, 24, 3161 (1946), with flowsheets and schemes of reactions.

Of the halogen derivatives, known commercially as Brilliant Indigos, those containing bromine give increasing green shades, while the chlorindigos lie between indigo and bromindigo in brilliancy.

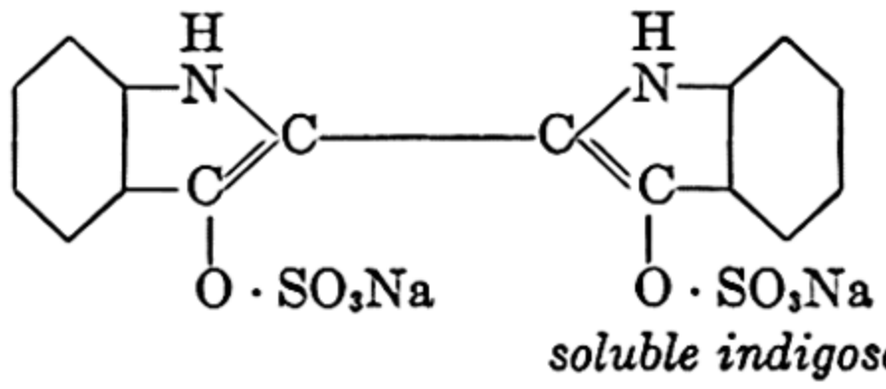
Bromindigos are prepared by the direct bromination of indigo with liquid bromine in acetic acid, or by refluxing in nitrobenzene.

The direct chlorination of indigo is performed in glacial acetic acid or nitrobenzene suspension, and is less simple.

Indigo is produced in the form of a 20 per cent paste, for domestic and export consumption. In 1930, 24,327,000 pounds of synthetic indigos were produced in the U. S.; in 1945, 13,390,000 pounds (16 cents) were produced, an increase over the 1940 figure of 11,133,161 pounds. In 1946, the production was up sharply, to 22,349,000 pounds (17 cents); in 1947, it was 25,805,000 pounds, valued at 20 cents a pound. The production of bromindigo blue 2BD, 16 per cent paste, in 1946 was 3,417,000 pounds (38 cents).[22]

Indigosols (IG), Soledons (ICI). These are later developments in the Indigoid and Vat classes of dyestuffs and are popular because of the ease of their application compared to the usual vat dye methods. The dyes are dissolved in water and are applied to the fiber. The fiber is then treated with an acid oxidizing liquor which develops the true vat dye in the fiber.[23]

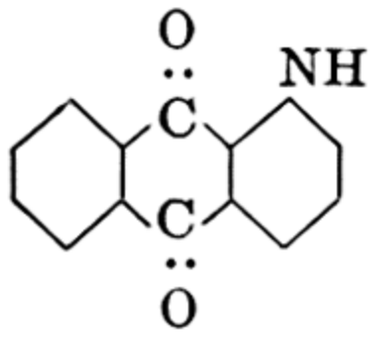
Indigo, for example, is applied in the form of soluble indigosol to the



soluble indigosol

fiber, then is treated with a solution of sodium nitrite or sodium bichromate when it reverts to the insoluble form of indigo.

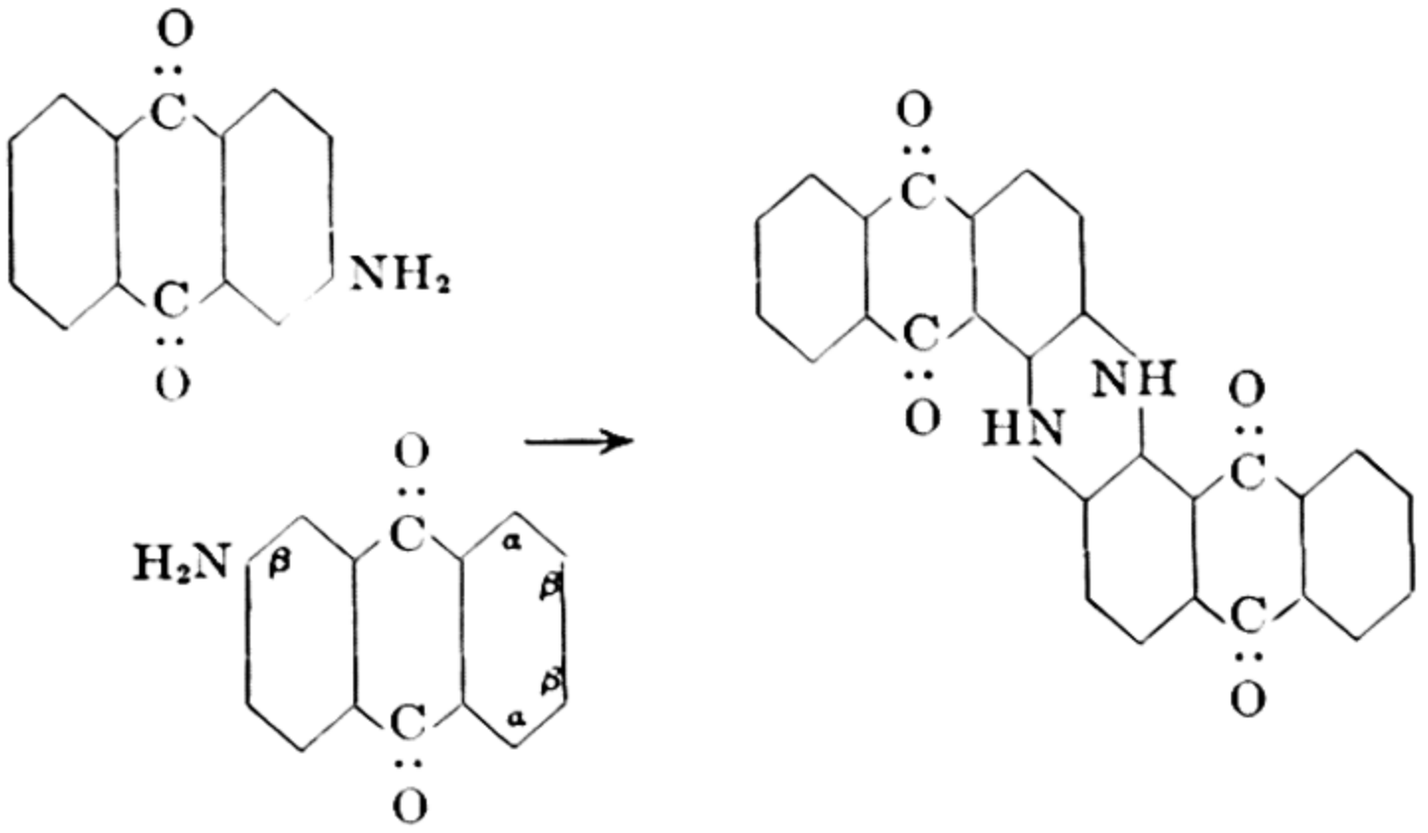
The Quinonoid Group comprises anthraquinonoid and other polycyclic quinonoid dyes. Some anthraquinone vat dyes are made from α- or β-aminoanthraquinone which are made by treating α- or β-anthraquinone sodium sulfonate with ammonia under pressure. The simplest of these dyes is Algol



Algol Yellow

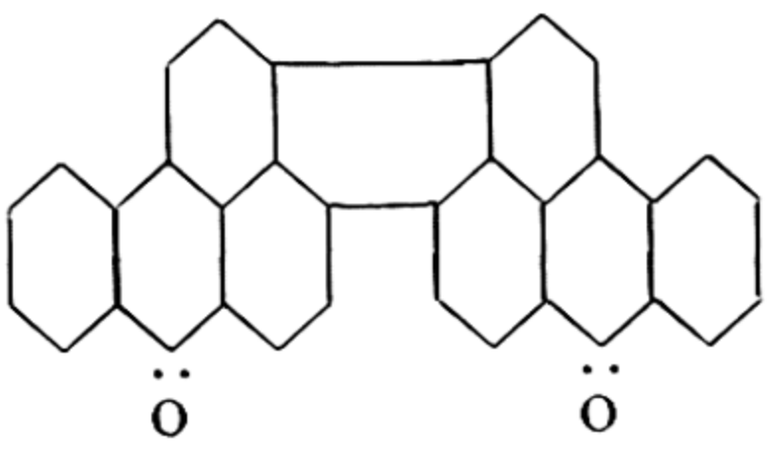
Yellow. By fusing β-aminoanthraquinone with caustic potash, Indanthrene is formed, a beautiful blue vat dye which when chlorinated is one of the fastest dyes known at present. To this class belong also Flavanthrene (yellow), Indanthrene Gold Orange, and the important phenanthrones.

[22] U. S. Tariff Commission, reports on Dyes.
[23] Brit. Patents 186,057; 313,407; 503,699.

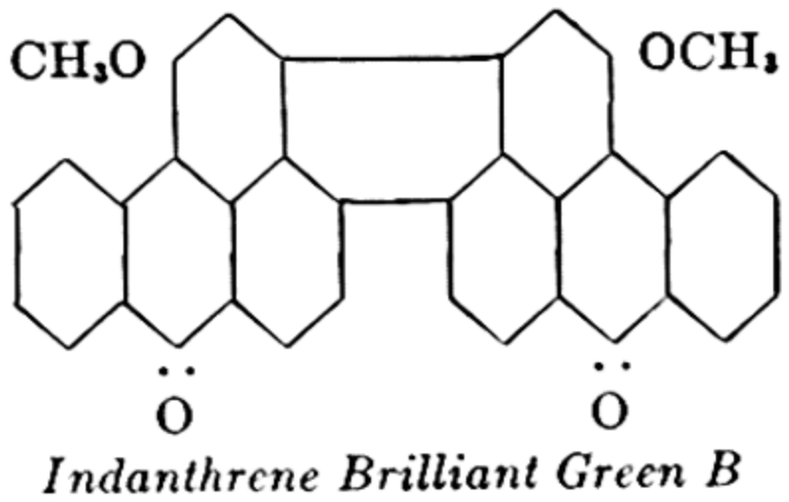


β-aminoanthraquinone (2 mols) → *Indanthrene* (blue)

Dyes of more polycyclic character are derived from Benzanthrone, such as



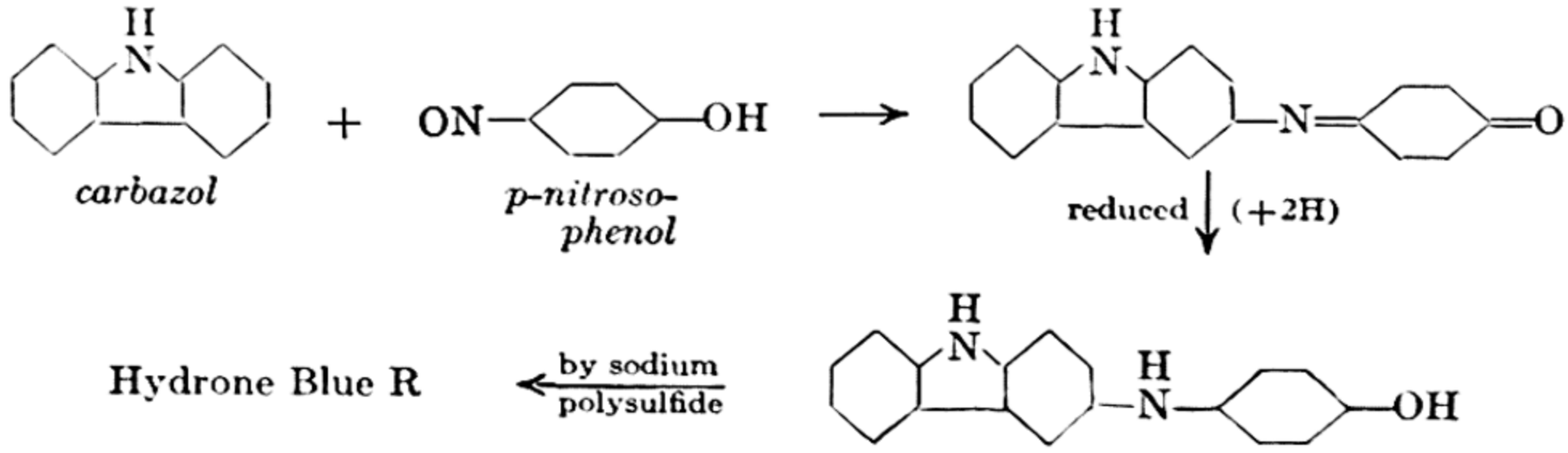
Indanthrene Dark Blue BO (Dibenzanthrone)



Indanthrene Brilliant Green B

Many dyes of this class are exceptionally fast, so that nowadays the term "vat dye" is synonymous with fastness.

Hydrone Blue is a class of sulfur dye which may be reduced by sodium hydrosulfite ($Na_2S_2O_4$) without destruction, unlike the typical sulfur dyes. In order to prepare Hydrone Blue R, para-nitrosophenol is condensed with carbazol in the presence of sulfuric acid at a definite temperature; the product is fused with alkali polysulfide. The formula of the dye is not fully known.



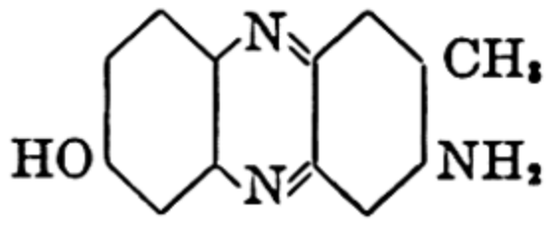
carbazol + *p-nitroso-phenol* → reduced (+2H) → Hydrone Blue R ← by sodium polysulfide

Hydrone Blue G is made from ethyl carbazol ($-N-C_2H_5$ instead of $N-H$) by condensing it with *p*-nitrosophenol; it gives a greener blue than Hydrone Blue R. Like the other vat dyes, Hydrone dyes must be reduced (sodium hyposulfite $Na_2S_2O_4$) in order to apply them to the fiber.

Sulfur Dyes

Many, but not all of the sulfur dyes are insoluble in water; they are reduced by sodium sulfide and thereby all of them become soluble, so that they can be applied to the fiber; they are reoxidized to an insoluble compound on exposure to the air. The constitution is essentially unknown, but the proper raw materials and the conditions for obtaining definite colors are fairly well settled.

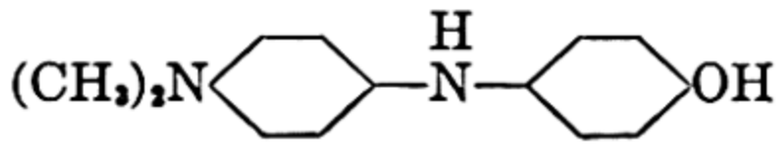
Meta-diamines, for instance metatoluidinediamine, fused with sulfur cause the evolution of hydrogen sulfide and produces a melt which yields brown and yellow dyes. Redder shades are obtained by using derivatives of azine; thus the methyl-aminooxyazine shown below,



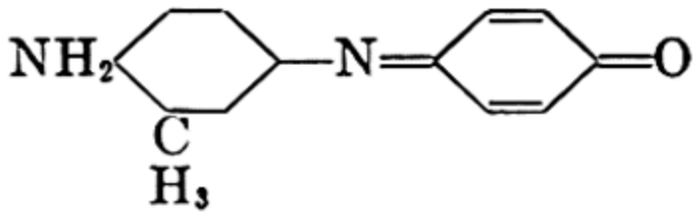
fused with polysulfide in presence of a copper salt, gives a Bordeaux color.

Blue shades are obtained by treating diphenylamine derivatives in alcohol solution with sodium polysulfide; a water solution may be used also.

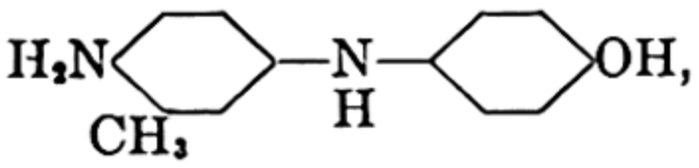
From



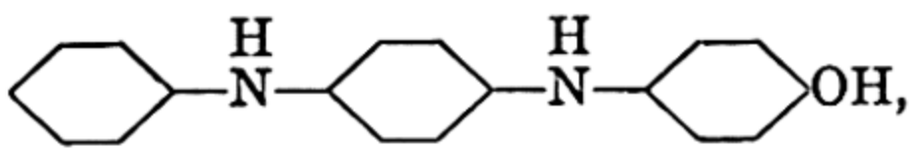
there is obtained Immedial Sky Blue. By condensing nitrosophenol and ortho-toluidine in 80 per cent sulfuric acid there is formed the body



which can be reduced to the leuco compound

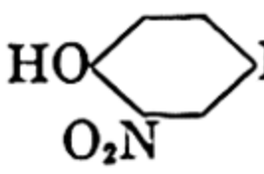


the latter, treated with polysulfide in alcohol, gives Thionone Indigo. Similarly the condensation product of nitrosophenol and diphenylamine, with the formula



yields Pyrogene Indigo.

On refluxing in water or by heating under pressure meta-dinitrophenol



with polysulfide, Sulfur Black is formed.

In order to isolate the dye, the procedure is to dissolve the melt in water and blow in air till all the dye has separated; it is filtered, washed, and dried in circulating air driers.

Dyes for Synthetic Resin Products

A spirit-soluble dye is made by condensing a water solution of a sulfonic acid dye in an acidified solution with a base, such as diphenylguanidine.[24]

[24] U. S. Patent 1,674,128.

In order to bring about the reaction, the bath may have to be heated to boiling, or it may not require any heating. A precipitate is formed which is sometimes tarry. The clear liquid is decanted, and the precipitate dried, preferably under reduced pressure. Extensive use is made of these spirit-soluble dyes for coloring synthetic molding resins, for which they are well adapted, as they dissolve readily in them. They are soluble in organic solvents.

Just which dyes will be suitable for the diphenylguanidine treatment cannot be told before a trial; the only general statement which can be made is that any dyestuff containing an acid group in its molecule, so that its sodium salt will be water-soluble, is worth a trial (acid colors, a few direct colors, chrome colors, and Neolans).

Other dyes suitable for use with synthetic resin products are found among the oil-soluble dyes, azo or anthraquinone dyes without the salt-forming and solubilizing groups SO_3H and COOH and others.

Dyes for acetate rayon are used in cellulose acetate plastics, giving clear brilliant shades.

Permitted Coal-Tar Food Dyes. The "Food, Drug and Cosmetics Dyes" may be used for the artificial coloring of foodstuffs and beverages, provided they contain a minimum of 82 per cent of the pure coal-tar dye, and only a certain amount of specified impurities and moisture make up the remaining 18 per cent. The tests which must be used to establish the presence, absence, or quantity of the impurities are those which are published in the official bulletin.[25] A selection of F. D. & C. items follows:

F. D. & C. Red No. 1, or Ponceau 3R $C_{10}H_{16}N_2S_2Na_2$, a mono-azo dye, made by diazotizing crude ψ-cumidine and coupling with R acid; a dark red powder, giving a cherry water solution.

F. D. & C. Red No. 4, or Ponceau S X $C_{18}H_{14}N_2O_7S_2Na_2$, a mono-azo dye, formed by coupling diazotized 1-amino-2,4-di-methylbenzene-5-sulfonic acid with 1-naphthol-4-sulfonic acid. It is a red powder, which dissolved in water gives red.

F. D. & C. Red No. 2, or Amaranth $C_{20}H_{11}N_2O_{10}S_3Na_3$, a mono-azo dye, made by diazotizing naphthionic acid and coupling with R acid; a reddish-brown powder, giving a magenta-red water solution.

F. D. & C. Red No. 3, or Erythrosine $C_{20}H_8O_6I_4Na_2$, the sodium salt of tetraiodofluorescein, a brown powder, which in water gives a cherry-red solution without fluorescence.

F. D. & C. Orange No. 1, or Orange I $C_{16}H_{11}N_2O_4S \cdot Na$, a mono-azo dye, made by coupling diazotized sulfanilic acid with α-naphthol; a reddish-brown powder, dissolving in water to give an orange-red solution.

F. D. & C. Yellow No. 6, or Sunset Yellow F C F $C_{16}H_{10}N_2O_7S_2Na_2$ is a mono-azo dye, formed by coupling diazotized sulfanilic acid with β-naphthol-6-monosulfonic acid; the powdered dye is orange-red, and dissolves in water to give an orange-yellow color.

F. D. & C. Yellow No. 1, or Naphthol yellow S $C_{10}H_4N_2O_8S \cdot Na_2$, a nitro dye, is the sodium salt of 2,4-dinitro-α-naphthol-7-sulfonic acid; a light yellow powder which in water forms a yellow solution, unaltered by either acid or alkali.

F. D. & C. Yellow No. 5, or Tartrazine* $C_{16}H_9N_4O_9S_2Na_3$, a pyrazolone dye; it is a yellow-orange powder, soluble in water.

[25] Bulletin 1390 and supplement No. 1, "Chemistry and analysis of the permitted coal-tar food dyes," by Joseph A. Ambler, W. F. Clarke, O. L. Evenson, and H. Wales, Color Laboratory, Bureau of Chemistry, U. S. Dept. Agriculture, 1927-1930. Since the passage of the Federal Food, Drug and Cosmetics Act, May 4, 1939, the dyes are designated by number, as shown; see Federal Register, vol. 4, No. 89, p. 1922, Washington, May 9th, 1939.

* Formula will be found elsewhere in this chapter.

F. D. & C. Yellow No. 3, or Yellow AB $C_{16}H_{13}N_3$, an oil-soluble mono-azo dye, is made by coupling diazotized aniline with β-naphthylamine; insoluble in water.

F. D. & C. Yellow No. 4, or Yellow OB $C_{17}H_{15}N_3$, an oil-soluble mono-azo dye, is made by coupling diazotized ortho-toluidine with β-naphthylamine; it is insoluble in water.

F. D. & C. Green No. 1, or Guinea Green B $C_{37}H_{35}N_2O_6S_2Na$, a triphenylmethane dye, is made by condensing benzylethylaniline-sulfonic acid with benzaldehyde, oxidizing, and converting the resulting product to the mono-sodium salt. It is a dull dark-green powder, dissolving in water to give a green solution.

F. D. & C. Green No. 2, or Light Green SF Yellowish $C_{37}H_{34}N_2O_9S_3Na_2$, a triphenylmethane dye, has the composition of Guinea Green B with an additional sulfonic acid group; it is a reddish-brown powder which in water forms a green solution.

F. D. & C. Green No. 3, or Fast Green FCF* $C_{37}H_{34}N_2O_{10}S_3Na_2$ is a triphenylmethane dye which is formed by condensing benzylethylaniline-sulfonic acid with para-hydroxy-ortho-sulfobenzaldehyde and oxidizing the resulting product. It is a reddish or brownish-violet powder, which when dissolved in water gives a bluish-green solution.

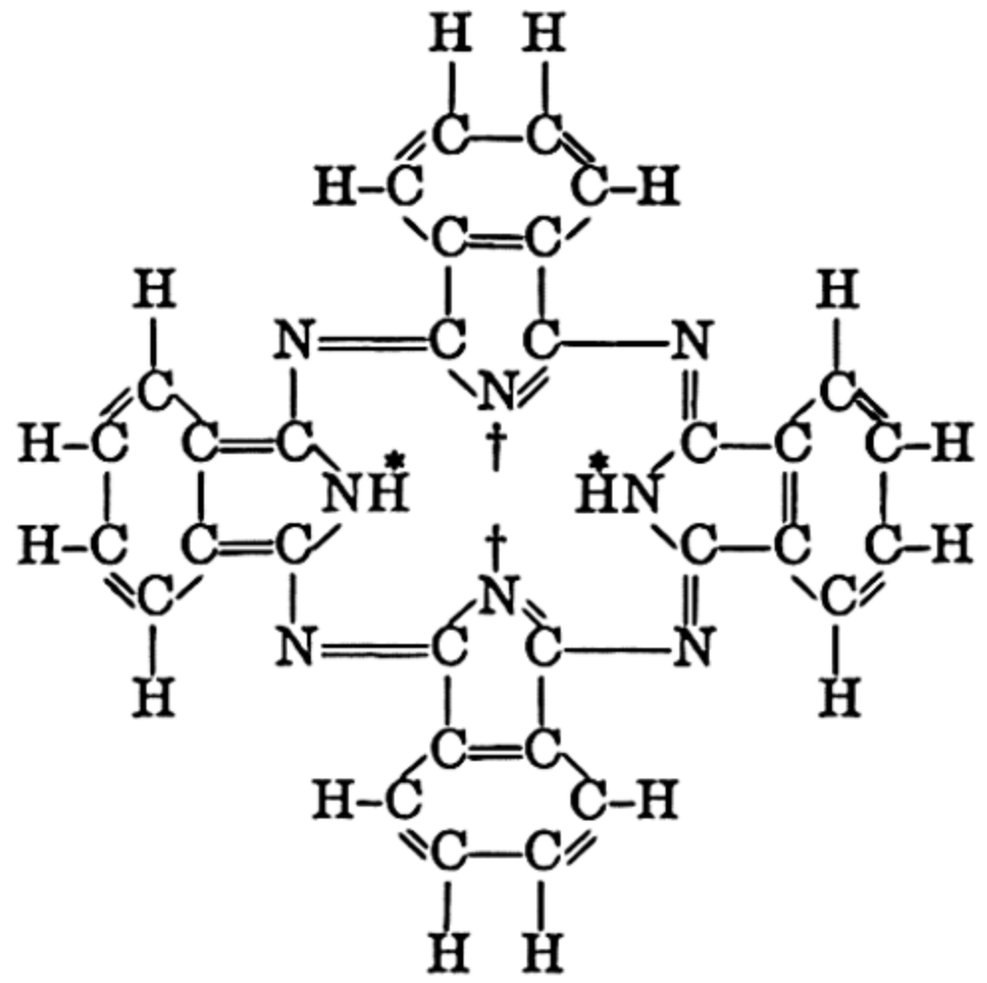
F. D. & C. Blue No. 1, or Brilliant Blue FCF $C_{37}H_{34}O_9S_3N_2Na_2$, the disodium salt of the triphenylmethane dye formed by condensing benzaldehyde-ortho-sulfonic acid with ethyl-benzylaniline-sulfonic acid; it is a dark purple bronzy powder which dissolves in water to form a greenish-blue solution.

F. D. & C. Blue No. 2, or Indigotine $C_{16}H_8N_2O_8S_2N_2$, is the sodium salt of the disulfonic acid of indigo,* made from synthetic indigo; it is a blue-brown or red-brown powder, which dissolves in water to form a blue solution.

These dyes are listed in the order of their absorption of light in the visible spectrum, beginning with the red end, and proceeding toward the blue.

In addition to the Foods, Drugs and Cosmetics Dyes, there is a list of Drug and Cosmetics Colors, which in 1946 included in its total the External Drug and Cosmetics Colors. The production in 1946 in the United States of Food, Drug and Cosmetic Dyes was 803,000 pounds, valued at $2.93 a pound, while the Drug and Cosmetics Colors totaled 172,000 pounds valued at $2.99 a pound.

Phthalocyanines. Phthalocyanines are a new class of synthetic pigments and dyes, actively developed between 1927 and 1937. They are blues and greens, with application in every field in which colored pigments are used. Their basic structure is:



* Formula will be found elsewhere in this chapter.

The unmarked hydrogen atoms can be replaced by a number of groups such as halogens,[26] sulfonic acids,[27] alkoxy,[28] aryloxy,[29] phenyl,[30] and many others. The two hydrogen atoms marked with a star can be replaced by metals such as lithium, sodium, magnesium, beryllium, nickel, copper, chromium, etc.[31]

Of this new class of compounds the copper phthalocyanine, in which an atom of copper is linked by primary valences to the two nitrogens bearing the starred hydrogens and by covalent bonds to the two nitrogens marked † in the formula above, is the most popular and is sold as Monastral Fast Blue BS. Its uses are numerous; for example, it is used in printing inks, and has superior fastness to older products; artists' color because of its brilliance and permanence; paints, lacquer and enamels, where it overcomes poor fastness to alkali of the iron blues and the poor fastness to acids of the ultramarines; water paints; coated textiles; paper; linoleum, because of its fastness to the harsh treatment received in linoleum manufacture; rubber; plastics, and textile printing.

There are a few solubilized phthalo-cyanines which are finding application in direct and mordant dyeing of cotton and are popular because of their brilliance.[32]

New Developments in Dyes. Other new developments in dyestuffs which are of major importance both as to value and quantity produced, are (1) the Neolan Dyes, (2) Celanese dyes, (3) Polar or Milling Dyes, (4) Hansa Yellows, (5) the Naphthols, (6) Stable Diazo Salts, (7) Rapidogen Dyes, and (8) Formaldehyde dyes.

(1) The Neolan Dyes (Soc. Chem. Ind. in Basel) or Pilatus Dyes (I.G.) are acid azo dyes containing a co-ordinated metal atom in the dye molecule.[33] It is a well known fact that "Chroming" dyes after they have been applied to the fiber by the addition of chromium salts to the exhausting dyebath increases their stability or fastness to light and washing.

These new dyes are azo dyes made in the usual manner, except that before isolation the solution of the dye is treated with a chromium salt, such as chromium formate under reflux or pressure, and the dye is then isolated. As a result, the chromium salt of the dye is formed before application to the fiber, eliminating the necessity of a two-step operation during the dyeing. The fastness to light and washing is as good as can be obtained with the older method of dyeing.

(2) Fabric made from cellulose acetate or acetate rayon, cannot, as a rule, be dyed with the ordinary cotton or wool dyes. In recent years, with the

[26] French Patent 815,088, 7/5/37; British Patent 461,268, 2/15/37; British Patent 390,149, 3/22/33.

[27] British Patent 457,796, 12/7/36; British Patent 460,147, 1/18/37.

[28] British Patent 470,703, 8/16/37.

[29] British Patent 469,139, 7/20/37; British Patent 470,499, 8/9/37.

[30] French Patent 811,933, 4/26/37.

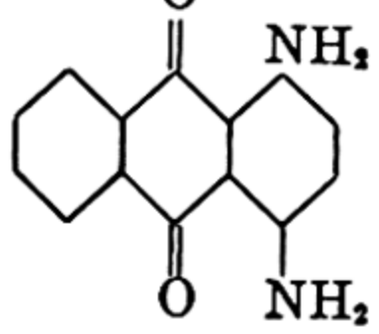
[31] British Patent 322,169, 11/18/29; British Patent 457,526, 11/30/36; British Patent 441,332, 1/13/36; British Patent 389,842, 3/22/32.

[32] Phthalo-cyanines: "A new Class of Synthetic Pigments and Dyes," by M. A. Dahlen, *American Dyestuff Rptr.*, 28, 603 (1939).

[33] British Patent 210,890 (1929); German Patents 369,584; 369,585; 433,148; U. S. Patents 1,693,448; 1,796,058; 1,844,396; 1,844,397; 1,844,398; 1,887,602; 1,893,557.

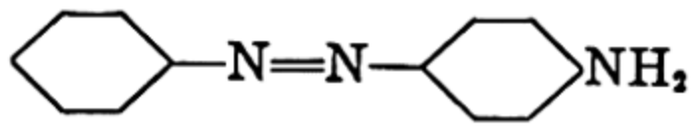
increase in popular use of cellulose acetate goods, a new group of dyes has been developed particularly for this textile.

The production of these, the Celliton (Gen.) Setacyl (Geigy), Celanthrene (Dupont), Nacelan (National) dyes with various other brands totaled 5.2 million pounds in 1946. They are made by dispersing water-insoluble organic compounds, usually basic in nature, by means of soaps or sulfonated fatty alcohols, into the colloidal state.[34] As colloidal particles these dyes can be applied to cellulose acetate. 1-4 Diaminoanthraquinone



violet

and Amino Azo-benzene

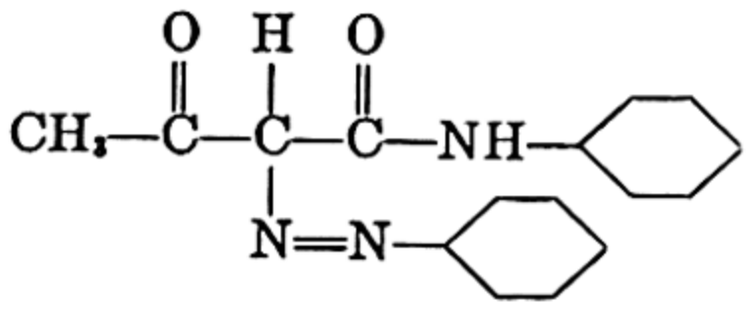


yellow

are typical compounds used in these dyes.

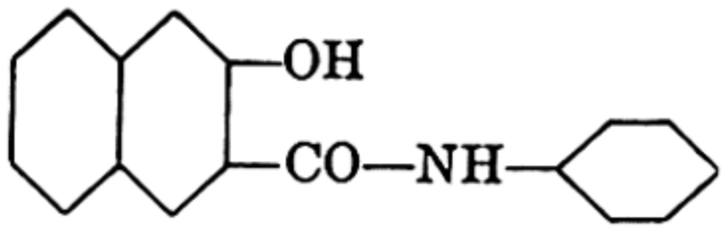
(3) Polar or Milling colors are used on woolen fabrics, such as bathing suits or rugs which are subjected to sunlight and wear. They are dis-azo dyes, the third component being a phenol, which is further condensed with para-toluol-sulfonyl chloride, markedly increasing the fastness to acids and sea water.[35] There are many other structures besides those mentioned.

(4) An important advance in the pigment field has been the introduction of the Hansa Yellows.[36] These colors are clear, bright, light-fast yellows, in many respects better than the inorganic chrome yellows when used for lacquers or paints. They are azo dyes made by diazotizing amines, or nitro or chlornitroamines, and coupling the diazonium compounds to acetoacetanilide or its derivatives.



Hansa Yellow

(5) The "naphthols," already presented in Chapter 26, are usually employed for developing Fast Salts and also components of Rapidogens and Rapid Fast Colors. They are arylides of beta-oxynaphthoic acid.[37] For example, Naphthol AS is



[34] U. S. Patents 1,448,432; 1,610,916; 1,618,413; 1,618,414.
[35] U. S. Patents 1,067,881; 1,602,776; 1,893,244; British Patent 26,908 (1913).
[36] U. S. Patents 1,059,599; 1,051,565; 1,644,003; 1,082,719.
[37] U. S. Patents 1,101,111; 1,935,554; 1,819,127; 1,971,409; 1,457,114. *J. Soc. Dyers and Colourists*, 40, 218 (1924); 96, 229 (1930).

Amines, other than aniline, can be condensed with the COOH group of the beta-oxynaphthoic acid in the presence of a dehydrating agent such as PCl_5, etc., forming other members of this popular series of dye intermediates. In physical appearance they are usually light tan.

They are dissolved in an alkaline solution and are applied or "padded" on the fiber which is then run through a solution of a diazo. Coupling takes place in the alpha position.

Using various numbers of the Fast Salts (stable diazo salts), shades on cotton from yellow to black are available. Colors made from the naphthols are usually insoluble in water and hence are used for pigments and textile printing.

Production of the naphthols for 1946 totalled 2,174,000 lbs.; for 1947, 2,528,000 lbs.

(6) With the naphthols came the development of the stabilized diazonium salts,[38] solutions of which can be used in place of preparing the diazo solution from the amine in the dyehouse. Their manufacture is described in an earlier paragraph. Production of these Fast Salts for 1946 (U. S.) was 726,000 lbs.

(7) The use of the naphthols and Fast Salts led further to the development of the Rapidogens [39] and Rapid Fast Colors described fully in Chapter 26.

These dyes compete with the vat dyes because of ease of application, which offsets the greater light-fastness of the vat dyes.

The Rapidogens, Fast Color Salts and naphthols as just described, are classed together under the term of Azoic dyes.

(8) **Formaldehyde Dyes.** The formaldehyde dyes constitute a new class of direct dyes,[40] which have very good washing fastness when after-treated with a solution of formaldehyde (10 per cent). They are, for the most part, direct dyes which have resorcin as an end component. After-treatment on

TABLE 108.—*United States production of coal-tar dyes, by chemical class, in 1947.**

	Pounds	Cost/Lb.
Azo dyes	78,054,000	.80
Sulfur or sulfide dyes	41,820,000	.31
Indigoid and thioindigoid dyes	36,146,000	.31
Anthraquinone vat dyes	25,490,000	1.26
Triphenylmethane and diphenylnaphthylmethane dyes	7,542,000	1.36
Anthraquinone dyes	6,687,000	1.45
Pyrazolone dyes	2,453,000	1.12
Ketonimine dyes (Auramine)	1,762,000	1.02
Stilbene dyes	1,482,000	.78
Xanthene dyes	943,000	2.55
Quinoline dyes	192,000	1.99
Acridine dyes	174,000	1.44
Oxazine days	50,000	1.45
All other	9,361,000	.78
Total	212,156,000	.72

* U. S. Tariff Commission.

[38] U. S. Patents 1,572,715; 1,975,409; German Patent 94,495.
[39] U. S. Patents 1,882,560; 1,882,561; 1,882,562; 1,858,623; 1,505,568; 1,505,569.
[40] U. S. Patents 1,087,430; 1,878,471; 2,204,230; 2,278,492.

the fiber with formaldehyde gives a dyeing with improved washing fastness by a simpler method than that used for developed colors (which are diazotized on the fiber and developed with β-naphthol, for example). The resorcinol coupling affects the shade only slightly.

Production and Uses. The production of coal-tar dyes is exhibited in the Tables 108 and 109. Their uses are listed after the tables.

TABLE 109.—*United States production of coal-tar dyes, by class of application, in pounds.**

	1947	1946	1941-45 Annual Average
Acetate rayon dyes	6,208,000		
Acid dyes	23,371,000		
Azoic dyes	7,947,000		
Basic dyes	10,314,000		
Direct dyes	43,480,000		
Lake and spirit-soluble dyes	6,303,000		
Mordant and chrome dyes	9,565,000		
Sulfur dyes	41,820,000		
Vat dyes	60,797,000		
of which indigo	25,850,000		
All other	34,992,000		
All other coal-tar dyes	2,351,000		
Total	212,156,000	186,307,000	152,283,000

* U. S. Tariff Commission.

Uses and Production. Dyes go to the textile industry, paper industry, leather, foodstuff, fur, pigment, synthetic resins, boot polish, printing ink, and many other industries. A color confined to one industry, for example, the woolen industry, would be standardized on wool; on the other hand, Nigrosine, Citronine, Resorcine Brown are tested on vegetable-tanned leather.

All dyes and dyestuffs, when isolated, have to be dried, milled and standardized. Drying is done mostly in circulating air driers, sometimes in vacuum shelf driers. Milling is done in a disintegrator, or ball mill. The diluents added are salt, anhydrous sodium sulfate, dextrin, and others.

For dyes which have a minimum of salt, pressing in a hydraulic press, for the removal of the greater part of the adhering water, is coming into general use.

Also of interest is the fact that, at times, a second dye is a by-product, and must find an outlet; thus when one ton of Oxyphenine Yellow 2G is made, one ton of Primuline is simultaneously produced.

OTHER PATENTS

German Patent 145,373, on phenylglycine production; U. S. Patent 1,431,306, on brilliant indigo; German Patent 237,262, U. S. Patent 1,012,363 and 1,473,887, all on indigo derivatives; 1,877,800, manufacture of tri-azo dyes, and 1,821,290, of di-azo dyes; 1,848,228, method for making black and gray vat dyes, comprising the condensation of a sulfonated benzanthrone compound with hydroxyl amine, followed by alkaline fusion; 1,759,264, manufacture of new sulfur dyes; 2,029,313, production and application of new dyestuffs for cellulose ester and ether by means of an unsulfonated anthraquinone compound; 2,069,158, dis-azo dyestuffs, insoluble in water, a developed dye for cotton. Substantive, metallizable disazo dyes for cotton, wool, silk, rayon, U. S. Patent 2,411,646; anthraquinone dyes, Brit. Pat. 568,933, April 26, 1945; anthraquinone vat dyes

for wool, silk, leather, cotton, linen and rayon, Brit. Pat. 585,874, see C. A. 41, 7129; tablets for dyeing textile products, Dutch Pat. 57,366, April 15, 1946, see C. A. 41, 4653; sulfur-containing dyes for cotton, Brit. Pat. 588,696, May 1947.

Problems

1. Azo dyes are manufactured from a bill of materials which lists the pounds of the various ingredients, their percentage purity, the molecular weight, the mols used, and the molecular equivalents represented. The molecular weight is the theoretical one, but the mols used and therefore the mol equivalent includes the excess necessary to drive the reaction to an end, or to exhaust any certain ingredient. Such a list includes items for caustic, soda ash, acids, sodium nitrite and other inorganic chemicals. Working in a simpler way; set up the bill of materials which are required to make 924 pounds of Direct Blue 2B, assuming that the yields are perfect, and that theoretical quantities will lead to a complete reaction.

Start with the proper weight of benzidine; make it into diazotized benzidine, then follow the description in text.

2. The yield of indigo powder based on the phenyl glycine, let us assume to be 75 per cent. How much indigo blue and from it, indigo white will be obtained from 600 pounds of glycine? How much sodamide will be required, and how much indoxyl is formed? The hydroxides used are twice the weight of the potassium glycine; what size pot will be large enough to allow the fusion? The general shape should be as indicated by the fusion kettle in Chapter 27.

Reading References

"Colour index," F. M. Rowe, Society of Dyers and Colourists, 32 Picadilly, Bradford, Yorkshire (England), 1924. A revised edition is about to appear.

"Farbstofftabellen," Dr. Gustav Schultz, 1914, reproduced by 42nd Street Commercial Studio, 138 W. 42 st., New York.

"Dyestuffs derived from pyridine, quinoline, acridine, and xanthene," J. T. Hewitt, a monograph, London and New York, Longmans, Green & Co., 1922.

"Fortschritte der Theerfarbenfabrikation und Verwandter Industriezweige," P. Friedlaender, for the years 1877 to 1925, in 14 volumes, published by Julius Springer, Berlin; a collection of German patents, classified in chapters with suitable introductions and summaries, and with comments as to their practical value. New volumes in preparation.

"Growth of the dyestuffs industry: the application of science to art," R. E. Rose, *J. Chem. Ed.*, 3, 973 (1926). Illustrated by 50 samples of colored cloth.

"From within the dyestuff industry," H. Levinstein, *J. Soc. Chem. Ind.*, 50, 251T (1931).

"Dyestuffs and their manufacture," J. Blair, *J. Soc. Chem. Ind.*, 51, 197 (1932).

"The synthetic dyestuffs and the intermediate products from which they are derived," J. C. Cain and J. F. Thorpe, London, Chas. Griffin and Co., 1933.

"A.S.T.M. (American Society for Testing Materials) standards on textile materials," prepared by Committee D-13 on Textile Materials, October, 1936, publ. by A.S.T.M., 260 Broad street, Philadelphia, Pa.

"Men and women's shoe and leather colors for spring 1937," *Dyestuffs*, 34, 209 (1936).

"Vynion: new textile fiber," Dr. F. Bonnett, *American Dyestuff Reporter*, 29, 116 (1940).

"Use of Fiberglas in textiles," P. W. Booker and Edward Ames, *American Dyestuff Reporter*, 30, 412 (1941).

"The theory and practice of wool dyeing," C. L. Bird, publ. Society of Dyers and Colourists, 32 Picadilly, Bradford (England) 1947, with chapters on acid dyes, chrome dyes, and Neolan and Palatine Fast Dyes.

"The insoluble Azo (Azoic) colouring matters (Part III), S. Yates, The Industrial Chemist (London), 20, 667 (1944).

"The chemical technology of dyeing and printing: Vat, sulfur, indigosol, azo and chrome dyestuffs and their auxiliaries," L. Diserens (translated by P. Wengraf and H. P. Baumann), New York, Reinhold Pub. Corp., 1948.

About 100 years ago the French chemist, Chevreul, demonstrated that oils and fats, such as olive oil and lard, are glycerides of fatty acids; on this knowledge as a basis the handling and refining of edible oils and fats was remodeled. Some twenty years ago two French scientists, Sabatier and Senderens, made another important contribution to this field when they transformed oleic acid, an oil, into the solid stearic acid; technologists from every land have constructed a number of devices based on this reaction, so that the "hardening" of edible oils into edible fats is now a well-established branch of this industry.

Chapter 29

Animal and Vegetable Oils, Fats, and Waxes

The animal and vegetable oils, fats, and waxes are esters of organic acids belonging to the fatty acid [1] series. An ester is formed by the combination of an alcohol and an acid, with the elimination of water. The animal and vegetable oils and fats are glycerin (really, glycerol) esters of a wide variety of fatty acids, in which the glycerin is the alcohol; the waxes are esters of the same kind of acids, but the alcohol is some other one instead of glycerin. The fatty acids belong chiefly to three or four subdivisions: to the saturated series (stearic acid), to the oleic series (which is unsaturated, lacking two hydrogen atoms), or to more unsaturated series lacking four and more hydrogen atoms.

The glycerides of the saturated series melt higher than those of the oleic series. A fat is rich in glycero-stearate, and has some glycero-oleate admixed; an oil would be rich in glycero-oleate and poor in glycero-stearate. But among the glycerides of the saturated acids, a further consideration must be made. One molecule of glycerin requires three molecules of acid to form an ester. If the three acid residues are the same, the fat is rather hard; thus glycero-tristearate, called stearin for short, melts at 72° C.; if the three acid residues are unlike, the fat has a lower melting point; thus glycero-distearate-monopalmitate melts at 63° C.

$$\begin{array}{l} CH_2—OH \\ | \\ CH—OH \\ | \\ CH_2—OH \end{array} + 3C_{17}H_{35}COOH = \begin{array}{l} CH_2—O—OC\,.\,H_{35}C_{17} \\ | \\ CH—O—OC\,.\,H_{35}C_{17} \\ | \\ CH_2—O—OC\,.\,H_{35}C_{17} \end{array} + 3H_2O$$

glycerin (an alcohol) — *stearic acid* — *glycero-tristearate* (an ester)

In each oil and fat, a number of different fatty acids occur, sometimes as many as ten, six or more being the rule; this would make the study of the composition of an oil difficult enough. The complications of mixed esters such as glycero-distearate-monopalmitate increase the difficulty still more; it is therefore not surprising that there are many oils and fats whose composition is still unsettled.

The study of the composition of the oils and fats is based on a knowledge of the constituent fatty acids, a number of which are listed in Table 110,

[1] It is because of their presence in fats that these acids have been named fatty acids.

with the names of oils and fats in which they occur; the latter are merely examples, for each fatty acid occurs in a large number of oils and fats.[2]

TABLE 110.—*Fatty acids occurring in the form of esters in oils, fats, and waxes.**

		Melting point of the free acid	Melting point of the simple triglyceride	Chief occurrence
Group A—Saturated Series				
Butyric	$C_4H_8O_2$	liquid	liquid	butter fat 4%
Capric	$C_{10}H_{20}O_2$	31.3° C.	liquid	butter fat, coconut oil
Lauric	$C_{12}H_{24}O_2$	43.6	45	coconut oil 45%
Myristic	$C_{14}H_{28}O_2$	53.8	56.5	butter fat, 22%
Palmitic	$C_{16}H_{32}O_2$	62.6	65	palm oil, lard
Stearic	$C_{18}H_{36}O_2$	69.3	72	all fats
Carnaubic	$C_{24}H_{48}O_2$	74	—	carnauba wax
Cerotic	$C_{26}H_{52}O_2$	78	76.5	beeswax
Mellissic	$C_{30}H_{60}O_2$	90	89	beeswax
Group B—unsaturated, lacking two hydrogen atoms				
Oleic	$C_{18}H_{34}O_2$	14	liquid	olive oil 70%
Erucic	$C_{22}H_{42}O_2$	33	31	rape oil; fish oil
Group C—unsaturated, lacking four hydrogen atoms				
Linoleic	$C_{18}H_{32}O_2$	—	—	cottonseed oil, linseed oil soyabean oil, tung oil
Group D—unsaturated, lacking six hydrogen atoms				
Linolenic	$C_{18}H_{30}O_2$	—	—	linseed oil 10%, tung oil
Isolinolenic	$C_{18}H_{30}O_2$	—	—	linseed oil 60%, tung oil

Note: "Coconut 45%" means that of the fatty acids present in coconut oil, 45% are lauric acid.
* Mainly from J. Lewkowitsch, "Chemical technology and analysis of oils, fats, and waxes," 3 vols New York and London, Macmillan Co.

The most important vegetable oils are cottonseed, linseed, soybean, olive, corn, peanut, rape, coconut, palm, and castor. The method of extraction is similar for all. The fruit or seed after cleaning by sieving and blowing, or by hand selection, is crushed and first cold-pressed for the highest grade, then pressed warm for technical grades; the crushed mass may be extracted still further by solvents. In the case of edible oils, the first grade is used for food purposes; the lower grades are used for technical purposes, including the making of soap. In order to be edible an oil must be attractive; it must possess an agreeable flavor (olive oil) and must be free from disagreeable odor. It must be pale in color, usually yellow; it may be without attractive odor, yet be wholesome and well suited for food. The oils used as salad oils in the United States are olive oil, mainly imported, corn oil (Mazola), peanut oil, and cottonseed oil (Wesson oil). The chief use of linseed oil is in varnishes and paints; of rape oil in lubricants, coconut and palm oils mainly in soap-making. Soybean oil, a comparative newcomer, is available in edible grade as well as technical grades suitable for the vehicle in paints, and for other purposes. Vegetable fats are mostly artificial, being made from the oils, such as cottonseed oil, by hydrogenation.

Animal oils and fats are: whale oil and fish oil (both less important now than formerly), by hydrogenation of which, fats are formed, which are

[2] Except butyric acid, which is characteristic for butter fat.

used in part for soap stock; lard and lard oil, for food; beef, mutton, and sheep tallow; fish-liver oils for pharmaceutical purposes; sperm oil, a liquid wax, for lubrication. The method of extraction is essentially a warming so that the oil may run off or be pressed out. Well-known waxes are carnauba wax and beeswax.

It will be noted that nothing has been said about distilling; none of the oils and fats can be distilled under atmospheric pressure without at least partly decomposing. They are called fixed oils, in distinction from the odoriferous oils described in the following chapter under the general name of essential oils, which are frequently distilled. The oils obtained from petroleum may also be distilled, but they remain well characterized as one group because of their mineral origin. In discussing paints and varnishes, the point of view of the varnish maker is adopted, who thinks of oils as drying, semi-drying, or non-drying. It is the state of unsaturation indicated for certain fatty acids in Table 110 (groups *C* and *D*), which permits the so-called drying because of oxidation by the air [3]; it is the same unsaturation which is relieved in another fashion by hydrogenation.

To compare successive shipments of the same oil, and to detect adulteration, a number of tests are applied, some of which are very old. In the Maumené test, the heat caused by the addition of sulfuric acid is measured. The saponification test records how much potassium hydroxide is consumed in forming the potassium salt of the fatty acid; an admixed mineral oil would not consume any caustic and would thereby be detected. The iodine value gives a measure of the unsaturation. Specific gravity and the refractive index in conjunction with the tests named above, and at times confirmable by specific tests, permit identification of the oil and estimation of its purity.[4]

The color of oils is lightened by adding fuller's earth, bone char, precipitated silica or similar finely divided substances, followed by filtration.

The extraction of linseed oil will be described in detail; the procedure for other seed-oils is similar.

Linseed Oil

Linseed oil is made by pressing warmed flaxseed [5] which has been previously crushed. Flax is grown in several northwestern states, notably in North Dakota, Montana, Minnesota, and South Dakota. Most of it, however, is imported from Argentina, so that linseed oil refineries are located at ocean ports as well as at inland points. The main product is the oil, but an important by-product is the press-cake, which forms a valued cattle food.

The flaxseed is stored in elevators very much as grain is. For the expression of the oil, the seed is elevated to the top of a five-story building so that in subsequent operations it may be fed by gravity. First it passes horizontal screens which remove all coarse admixed matter; then it is fed to a rotary bag blower with numerous small conical bags. These are connected period-

[3] *Compare* under varnishes in Chapter 31.

[4] "Standard methods of chemical analysis," W. W. Scott, New York, D. Van Nostrand Co. "Chemical technology and analysis of oils, fats, and waxes," J. Lewkowitsch, London and New York, Macmillan Co. "Vegetable Fats and Oils," G. S. Jamieson, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), 1932.

[5] Formerly called linen seed.

ically and automatically with compressed air, which blows out the chaff and small dirt. The clean seed is carried by a screw conveyor to one of a number of large storage bins; the crushing rolls are situated under them on the next floor. Flaxseed is so slippery that if a man steps into a tall bin he will go through the seed to the bottom. The seed is small, about 3 mm. long, 2 mm. wide, and 1 mm. thick, so that it will escape through the bottom of a farm wagon unless the boards are brought tight together.

The crushing device consists of 5 heavy steel rolls placed in a vertical line; the two upper rolls are corrugated. Three rolls are driven, the first, third, and fifth; the second and fourth are idle. The speed is 175 rpm. The seed from the bin is fed by gravity to the top roll; by means of small troughs, the meal is collected from one roll and fed to the next, making four passages in all. A completely mashed product results, which has lost all trace of shape.

The mashed meal passes by gravity to a two-stage, steam-jacketed kettle of moderate size, provided with slow agitation (30 rpm). The meal enters the kettle in the center of the first shelf, and passes to the second shelf through circumferential openings. It is drawn from here onto the filter press plates (generally horizontal) of a hydraulic press, with hair mats above and below each plate charge. When the press is closed (30 shelves), the oil runs off into gutters to a main trough in the floor, and from there to collecting tanks. The press cake, resembling a stiff board and still retaining 5 to 6 per cent of oil, is broken into small pieces by a rotating cylinder with projections, and then made into a powder in squirrel-cage disintegrators, rotating at extremely high speeds.

The hydraulic press method has been partly superseded by the oil expeller, generally two-stage, in which rotating screw elements (worms) compress the cake against a grid of heavy steel bars, forming a cage, through the spacings of which the oil escapes, while the worm moves the pressed cake to the discharge point. Unlike the hydraulic press, the operation of the oil expeller is continuous. Expellers are usually set up in batteries of 4, 8, 10 or any number; the mashed meal from the crusher moves along in an overhead screw conveyor, with down spouts to the pressing machines. Each expeller consists of a horizontal cooker, surmounting a short vertical worm and cage (the hopper feeder), which itself surmounts the main horizontal worm barrel (see Figure 224). In the steam-jacketed cooker, the meal is moved by a screw conveyor to the first, vertical barrel in which the worm turns at perhaps 46 rpm, compressing the seed and delivering oil, which runs off through the spaces in the grid. The partly pressed meal now enters the main, horizontal barrel, wherein the pressing is continued with the worm turning at perhaps 20.6 rpm, the oil running off to the horizontal gutter. The cake is discharged at the far end and is made into pressed cake meal, having an oil content of not more than 3.7 per cent in a 10 per cent moisture cake. It is high in proteins and is a valuable livestock feed, which has become so important that the fluctuations in its price are reflected in the price of linseed oil.

The expeller method has the advantage of lower operation labor cost over the hydraulic press method.

The importance of linseed oil is reflected in the domestic disappearance figure in the general table for fats and oils; the quotation for raw linseed oil in drums, carload lots (December, 1948) was 29.2 cents a pound.

Refining the Oil. The oil from the press, filtered through duck and flannel filter cloths in a plate-and-frame press, is the raw linseed oil of commerce; its color is a yellow-brown.

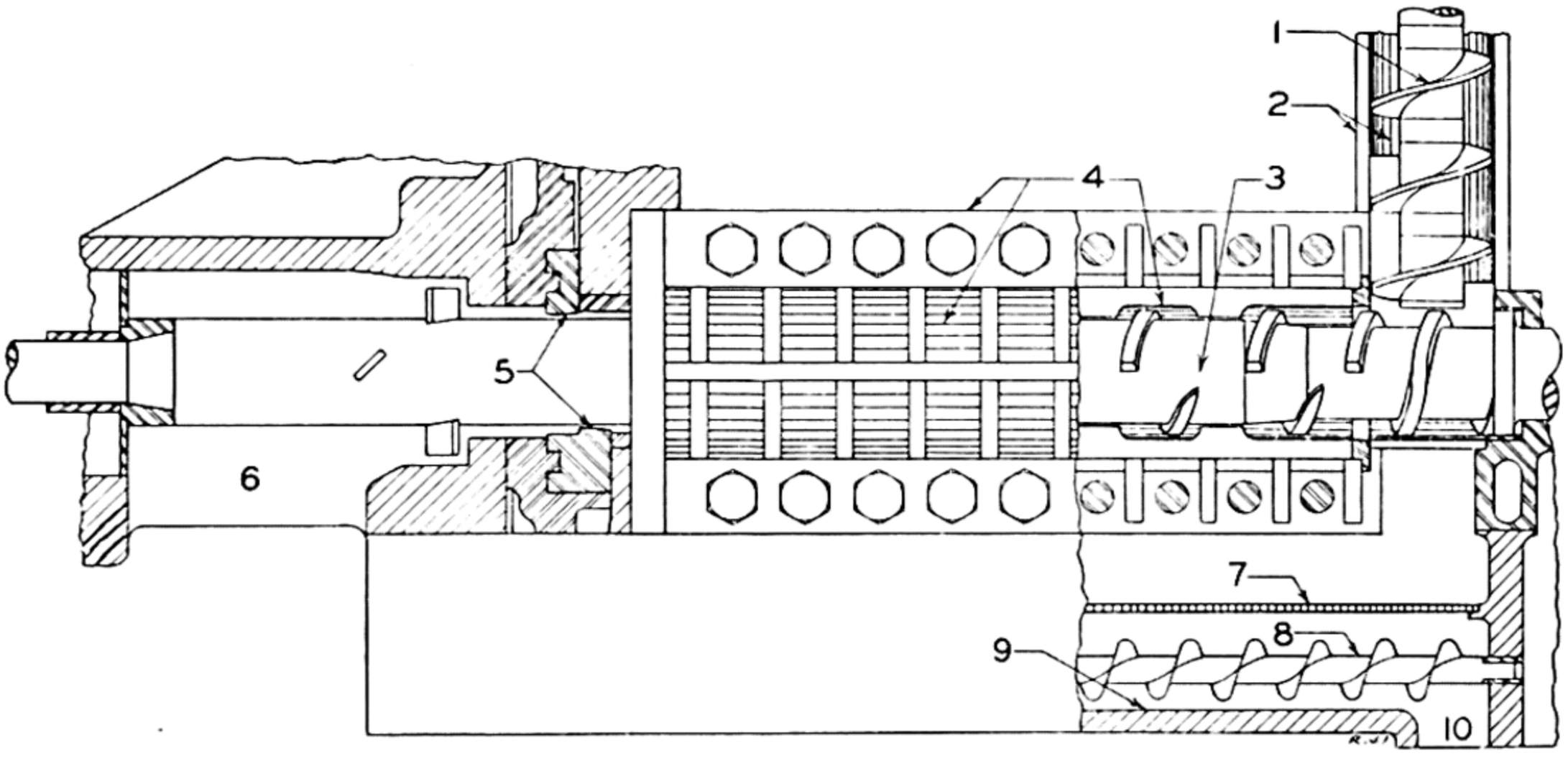


FIGURE 224.—The working principle of the Anderson expeller: (1) Vertical wormshaft unit, which receives the warm crushed seed from the cooker (not shown); (2) vertical barrel and spaced barrel bars; (3) horizontal integral main wormshaft (note interrupted flights); (4) horizontal barrel and spaced barrel bars; (5) upper and lower choke jaws; (6) discharge of exhausted cake in chip form; (7) screen for collection of settlings; (8) crude oil expeller screw; (9) bed for oil collection; (10) crude oil exit. (From sketches obtained from the V. D. Anderson Company, 1935 W. 96, Cleveland, O., with slight modifications.)

Large quantities are refined further by gentle heating for definite periods to remove moisture, and by adding fuller's earth followed by filtering through duck, flannel, and thick paper. The heating must be carefully regulated in order to avoid darkening the oil. The effect of the fuller's earth is partly to bleach the oil, partly to assist in the removal of finely suspended matter, called the "foots." For many purposes the oil must be "blown" to give it body, that is to raise the viscosity. This may be done by heating with steam coils and blowing in air for certain periods. The blowing is usually followed by a filtration.

Although linseed oil will "dry," that is, harden on exposure to air, through oxidation, such drying is too slow for practical purposes. The drying is greatly accelerated by adding small amounts of the oxides of lead, manganese or cobalt,[6] and then heating the oil under reduced pressure; the product is "boiled linseed oil," which dries in a few hours. The metals act as catalysts of the oxidation.

[6] Three-tenths per cent lead oxide, 0.1 per cent manganese dioxide, or 0.05 per cent cobalt oxide have the same accelerating power; a mixture of any two is still better. Iron oxide is also effective but it is not favored because it discolors the oil.

When fresh, linseed oil is edible; for that purpose it is expressed cold, and that is done to some extent on the continent of Europe. The chief use for linseed oil is as a vehicle in paints, varnishes and enamels.

Not only flaxseed, but many other seeds are pressed for their oil in the hydraulic press or the expeller. Large amounts of soybean oil are produced by pressure, but a part is extracted from the bean by means of solvents. One of the advantages of solvent extraction is that a more nearly exhausted residue is left; the extracted meal contains only about 1 per cent of oil, compared with the press cake and press meal with 5 to 6 per cent. At times when the oil is in great demand, this advantage would weigh heavily.

Vegetable Oils

Olive Oil. Because of its flavor, olive oil is the most highly prized of the edible oils. The olive tree is cultivated in Italy, southern France (Provence), Spain, Algeria, Tunis, and southern California. In general, the fruit is picked just before it is ripe; its content of oil varies from 35 to 60 per cent. The pressing for the highest grade is done cold, sometimes with the stone, other times after the stone has been removed. The fruit is packed in muslin bags and placed in a cylindrical cage surrounded by a sheet-steel envelope to catch the squirting oil. A heavy cylinder is applied from above, with gradually increasing force applied by means of a hand-operated screw. The oil collects in the floor trough. The color is pale yellow.

The pulp is mixed with cold water and pressed again, best with hydraulic pressure, and a second quality of edible oil is obtained. Made up with hot water, still another quality of edible oil is secured. Finally the pulp is extracted with carbon disulfide, which gives a dark product suitable for soap making. There is a difference in composition in the various grades. The free fatty acids, resulting from hydrolysis, are less than 1 per cent in the highest grade, 5 per cent in the next grade, and as high as 20 per cent in the technical grade.

Olive oil contains mainly the glyceride of oleic acid, an unsaturated acid; it is a non-drying oil.

Peanut Oil. This oil is a very acceptable substitute for olive oil. It is obtained by pressing the peanut, or earth-nut, and is called in Europe arachis oil from the name of the plant, *Arachis hypogæa*. The seeds or nuts contain 43 to 46 per cent of oil. The shells and skins are removed, the nuts are ground in squirrel-cage disintegrators, and cold-pressed first, when 18 per cent of the oil is obtained. This grade is used for salad oil, and has a pleasant nutty flavor. Two more expressions at higher temperature furnish technical grades.

Corn Oil. When starch is made from corn (maize) there is obtained as a by-product the kernel, which, on pressing in the same way as flaxseed, yields an oil, and a press-cake which is a cattle food. The corn seed contains 50 per cent of oil; when it is pressed cold, a pale yellow product is obtained having a slight odor. This is removed by refining, and the oil finds a market as a salad oil, in part under the name of "Mazola" in the

United States. The lower grades are used for soap-making, and to a limited extent in paints and varnishes.

Palm Oil. The best grades of palm oil are edible. The fresh fruit is pressed slightly warm, and a pale yellow, butter-like material is obtained; its consumption is limited to the natives of West Africa,[7] where the palm *Elœis guineensis* grows. The greater part of the oil is obtained by allowing the fruit to ferment in holes in the ground, then either pressing the softened fruit, or boiling it in water and collecting the oil which rises. The oil so obtained is suitable only for technical purposes, largely soap-making. Several other varieties of palms are cultivated in South America, and worked for oil.

The palm kernels are collected separately and yield a soft fat, the palm-kernel oil, of different composition from palm oil. The kernels are generally imported to Europe and the United States and utilized with modern working methods.

Cottonseed Oil. The second largest production of vegetable oil in the United States is that of cottonseed oil; only the production of soybean oil surpasses it. Even so, the production of cottonseed oil is 4 times that of corn oil, 8 times that of peanut oil, and 70 times that of olive oil. Table 111 indicates the relative importance of a number of the more prominent items in the list of oils.

The cottonseed contains 20 per cent of oil. How much seed is available may be judged from the fact that two pounds of seed are available for each pound of cotton. The cottonseed shell is first freed from adhering short cotton fibers, the linters, an article of commerce of some importance. Next the shell is cut by rotary knives and separated from the seed proper in a wire-gauze basket which rotates, letting the seeds pass through and retaining the hulls. The decorticated seeds are crushed and pressed; crude cottonseed oil red or brown in color is obtained. It is refined by warming it with a solution of caustic soda which removes much of the color and neutralizes the free fatty acids. The caustic solution forming the lower layer is run off, and the remaining oil washed. On standing in the cold, solid glycerides separate, and are removed by filtering under pressure. The oil may be bleached further by adding fuller's earth and filtering; edible grades are prepared in this way. It is used to some extent as an oil, to a constantly greater extent for hydrogenation, which gives cooking fats. It finds considerable use in making butter substitutes. Formerly it was largely used for making hard soap; to some extent soybean oil has displaced it. Cottonseed oil is a semi-drying oil.

In addition to seed-pressing mills, plants for the solvent extraction of cottonseed are increasing in number. The main piece of equipment in such a plant is the extractor, a vertical cylindrical column with shelves which have alternately central and peripheral openings to permit the descending solid matter to pass.[8] A central shaft with arms and plows sweep the shelves at a very slow rate. The column is filled with solvent (here hexane),

[7] Except for a small quantity placed in some margarines for color.
[8] Allis-Chalmers Manufacturing Company.

TABLE 111.—*Domestic disappearance of primary fats and oils, oleomargarine, and shortening in the United States (1947).**

	Lbs.
Primary fats and oils, by principal use	
Food: Butter	1,626,000,000
Lard and rendered pork fat	1,953,500,000
Oleo oil, oleo stock, edible animal stearin, edible tallow	180,300,000
Total edible animal fats	3,759,800,000
Corn oil	253,300,000
Cottonseed oil	1,111,700,000
Olive oil, edible	16,700,000
Peanut oil	138,400,000
Soyabean oil	1,448,400,000
Total edible vegetable oils	2,968,500,000
Soap: Tallow, inedible, and grease	1,883,000,000
Palm oil	43,400,000
Fish oils	151,000,000
Marine mammal oil	11,800,000
Olive oil, inedible, and foots	100,000
Total slow-lathering oils	2,089,300,000
Babassu oil	17,800,000
Coconut oil	760,900,000
Kernel oils (palm, murumuru, tucum, ouricury-kernel oils)	9,900,000
Total lauric acid oils	788,600,000
Drying-oil Products: Castor oil, dehydrated	33,200,000
Linseed oil	575,500,000
Oiticica oil	12,600,000
†Tung oil	104,800,000
Perilla oil	low amount
Total drying oils	726,100,000
Other industrial products:	
Neat's-foot oil	1,200,000
Wool grease	21,300,000
Cod oil and fish-liver oils	16,300,000
Castor oil, No. 1 and No. 3	82,500,000
Rapeseed oil	5,500,000
Other vegetable oils, sunflower oil and 7 others	8,700,000
Total	135,500,000
Grand total, primary oils and fats	10,468,000,000
Oleomargarine, actual weight	715,500,000
Shortening	1,346,000,000

* The Fats and Oils Situation, August 1948, Bureau of Agricultural Economics, U. S. Dept. Agriculture.
† Very low during the war, with the lowest 3,600,000 lbs in 1943; the 1947 figure is about equal to the 1937-41 yearly average.

which enters near the base, and leaves, loaded with oil, near the top. The cottonseed mash is introduced near the top, travels downward, and is exhausted at the bottom. The treatment of the oil-rich solvent and of the exhausted mashed seed is not unlike the similar solution which has been discussed under linseed oil, or the description which follows under soybean oil.

Another solvent which has been used in seed oil extractions is isopropanol.[9]

In 1947, crude cottonseed oil in tanks was 22.2 cents a pound; the refined oil, in drums, at New York, was 28.8 cents; the corresponding figures for

[9] *Chem. Eng.*, p. 256 (Aug. 1947).

June 1948, were 35.4 and 42, respectively. In 1939, cottonseed oil was valued at 6.2 cents a pound; in 1933, at 3.23 cents.

The range of wholesale prices for domestic vegetable oil meals (exhausted) for the past two years is as follows:

TABLE 111a.—*Prices for domestic oil meals, per ton**
(Pressed or extracted residue).

	Cottonseed meal		Linseed meal		Soybean meal	
	1947	1948	1947	1948	1947	1948
High	$ 97.15	$ 97.60	$ 94.80	$113.75	$102.70	$110.25
Low	62.25	62.80	69.10	64.50	65.40	66.80
Average	78.20	77.80	82.90	77.24	83.76	86.49

Cottonseed meal, 41 per cent protein, bagged, Memphis; linseed meal, 34 per cent protein, bagged, Minneapolis; soybean meal, 41 per cent protein, bagged, Chicago.

* Bureau of Agricultural Economics, Division of Statistical and Historical Research, Dept. Agriculture.

The production of pressed and extracted cake in 1947 was 3,796,000,000 pounds.

The average yield in pounds of oil and by-products per short ton of seed for the period of 1938-1947, with the average price figure, was as follows: oil 314; pressed or extracted meal 900; linters 174; hulls 484; all in pounds; while the prices were, respectively, 13.2, 2, 3, 4.6 and 0.6 cents a pound.

Coconut Oil. The cocoa palm grows in South America, India, Cochin-China, in the Philippine Islands, and other countries. The fruit is imported in the dried condition under the name of copra. The oil is expressed at 60° C., and is edible, either as such or mixed in margarines. The press cake is a cattle food.

The production of coconut oil is next to that of linseed oil (for the United States).

Soybean Oil. The soybean has been the important crop in Manchuria for years. It was not raised in the United States to any extent until 1924, when its culture was recommended and vigorously promoted, so successfully that in 1935, the production stood at 39,637,000 bushels. It has increased still further since then. Over 30 states have soybean acreage; the four which head the list are Illinois, Missouri, Indiana and Iowa.

The soybean pod contains from two to four beans, which vary in size and color with the plant. The Manchurian edible soybean is of pale brown color, and about the size of a large pea. Other varieties include the U. S. No. 2 Yellow, the Virginia brown, the black soybean, and the domestic pale brown bean somewhat smaller than the best selected Manchurian edible. The soybean pod contains from 2 to 4 beans; the bean contains 20 per cent of oil on an average. The modern methods of expressing the oil are by the two-stage Anderson expeller (already discussed under linseed oil), by the hydraulic press, and by solvent extraction. A method for such extraction with specific reference to the soybean, but applicable to other beans and seeds, after preliminary study, is as follows.

The beans are cleaned, cracked, heated and then flaked on flaking rolls Extraction of the oil from the flakes takes place in the extraction tower; this is essentially an upright, vapor-tight steel box in which an endless belt

carrying baskets with perforated bottoms and solid sides moves slowly up one side and down the other, like a bucket elevator. The solvent is hexane. As the baskets travel upward, a stream of fresh solvent fed in at the top of the casing reaches the top basket, wets its flakes and dissolves the last of the oil, then drains through the bottom to the basket next below it, where the wetting and partial extraction are repeated. In this fashion, the solvent with its oil travels downward, while the flakes travel upward. The nearly exhausted flakes receive the fresh, hence most active solvent. The extraction here is countercurrent.

The oil-containing solvent collecting on the up side of the boot is pumped to the top basket on the descending side. The basket is freshly loaded with new, unextracted flakes, which are thus wetted and partly deprived of their oil. The liquid in the first basket drains through the perforation in the bottom to the second basket, and from there to the third, finally reaching the lowest one. The extraction here is on the concurrent principle. The oil-rich solvent is collected on the down side of the boot. In moving from the down side of the elevator to the upside, the baskets remain upright because they are free to swing in the chain and to retain the upright position. At the top of the up trip, the baskets dump their load of exhausted flakes to a conveyor for further treatment. A charge of fresh flakes is fed into the empty basket, which starts on its extraction trip once more.

The solvent-oil solution is screened, filtered, heated and flashed twice, once at normal pressure, the second time at a reduced pressure; it then enters a combination evaporator-distilling column, with vertical evaporator tubes in the upper part and bubble-cap trays in the lower part, with steam entering near the bottom. The oil discharged from the bottom is solvent-free; it is cooled and forms the crude soybean oil, which is stored, or shipped as such, or refined further. The vapors from the column and flash chambers are condensed, and the liquid solvent so recovered is used over again. The exhausted, solvent-bearing flakes travel to two steam-jacketed cookers, where the solvent is expelled, and thence to two further cookers operated at higher temperatures, in which the flakes are "toasted" in multi-floor kettles provided with agitator sweeper arms. Finally the flakes are cooled, ground and bagged for shipment, or mixed with other materials for special livestock feed.

The secret of the success of the process lies in the flaking, which exposes the bean material to the solvent, while producing a fragment having enough strength to prevent it from disintegrating to a powder. The mass in the baskets remains permeable to the solvent.

Some of the crude soybean oil is made into boiled soybean oil; much of it is made into oils for lacquers, light paints, enamels, ink oil, oil for chocolate coatings, and for a long list of other specific uses, all this in addition to the edible grade. The meal is made into pellets of various sizes (pea size, sheep size, and others), with or without additions, for livestock feed. Selected whole bean shipments are made into flour and other valuable products, for human consumption.

One of the methods for refining a crude vegetable oil is the *Solexol* process, in which propane under pressure is the solvent. Its dissolving power varies with temperature; at its critical temperature (200° F.) it dissolves the good oil only, leaving other materials undissolved. By varying (lowering) the temperature, a separation of materials is attained. Thus crude soybean oil will yield refined soybean oil, and separately, pigment-lecithin; by further fractionation of the refined oil, edible oil, paint oil, and a sterol concentrate are obtained. From a crude sardine body oil there may be separated medium iodine-number oil, high iodine-number oil, concentrated vitamin oil, stearin, color bodies and fatty acids.[10]

Castor Oil. Castor oil is obtained from the seed of the castor plant, *Ricinus communis*, which grows in the West Indies, India, and other tropical countries. The seed contains 45 to 50 per cent of oil. The best grade, the cold-pressed oil, is widely used as a mild cathartic. Other grades are valuable as lubricants, mixed with mineral lubricating oil. Castor oil is a non-drying oil; it is a plasticizer for Celluloid and for lacquers.

Soluble Castor Oil or Turkey Red oil is sulfonated castor oil. Concentrated sulfuric acid is mixed with castor oil at temperatures not exceeding 35° C.; after some time, a small amount of water is added, and the dilute acid formed, which separates as a lower layer, run off. The oil is washed with a sodium sulfate solution. Ammonia is added in amount insufficient to neutralize the remaining acid, but sufficient so that the oil gives a clear solution with water. The soluble oil is used extensively in the preparation of the fibers for dyes (Chapter 26).

Dehydrated castor oil was developed and manufactured over the war years 1941-1946 as a substitute or "lengthener" for tung oil, the importation of which was stopped by the Japanese war. Castor oil consists mainly of the triglyceride of isoricinoleic acid, which contains a hydroxyl group; the removal of a molecule of water should leave an unsaturation, which, together with the unsaturation already present, should give the resulting oil excellent drying properties. Such proved to be the result, and large amounts of castor oil were dehydrated by heating in a vacuum in the presence of a catalyst. Water vapors pass out in an amount equaling 5 per cent of the weight of the oil:

$$CH_3(CH_2)_4CH_2\cdot\overset{12}{C}H(OH)\cdot\overset{11}{C}H_2\cdot\overset{9}{C}H{:}CH\cdot(CH_2)_7COOH$$

Ricinoleic acid or *12-hydroxy-9-octadecanoic acid*

The dehydrated product consists of the triglyceride of 9,12-octadecadienoic acid, with two double bonds (17 to 26 per cent), and the triglyceride of 9,11-octadecadienoic acid (59-64 per cent), also with two double bonds,

$$CH_3(CH_2)_4CH_2\cdot\overset{11}{C}H{:}\overset{9}{C}H\cdot CH{:}CH\cdot(CH_2)_7COOH$$

9,11-octadecadienoic acid, with conjugated double bond

which are conjugated. The catalysts employed are suspended granules of

[10] Pamphlet, "Prescription for glycerides," The M. W. Kellogg Company, 225 Broadway, New York 7, N. Y. "The Solexol process," *Chem. Industries*, 59, 1016 (1946).

alumina, silica gel, or fuller's earth. Other processes employ sulfuric acid, phosphoric acid, or sodium bisulfate for the catalyst.[11]

Styrenated oil is an example of the efforts to copolymerize the monomers styrene, butadiene, and methyl methacrylate with linseed oil, for example, producing drying oils with superior hardening qualities and increased alkali resistance, which are attractively priced. *Maleated* oils are unsaturated oils, such as linolenic acid, which have been made to react with maleic anhydride (at 250° F.), with the production of a tribasic acid (the Diels-Alder reaction). The new acid may be esterified with a tri-, tetra-, or penta-functional alcohol to give an ester which carries unreacted functional groups which permit further reactions in the molecule, with desirable results. Polyfunctional alcohols are pentaerythritol (tetra-functional), sorbitol (hexa-functional) and mannitol, here applicable.[12]

Rape Oil. Rape oil, *Brassica campestris*, is cultivated in Europe; seeds are also imported from India, and oil from Japan. The seed has 40 to 45 per cent of oil; the treatment is similar to that of flaxseed, and the press-cake is a cattle food. Rape oil has non-gumming properties, and finds extensive use as a mixed lubricant, with mineral oil.

Sesame Oil. Sesame oil is of some importance in Europe. The sesamum seed is imported from China and India. The best grades are edible, either as salad oil or in margarine; the lower qualities serve for soap making.

Chinawood Oil (Tung Oil). The seeds (*Aeurites cordata*) in a nut the size of a small orange contain 53 per cent of tung oil. When it is pressed by native methods, 40 per cent of the oil is expressed. In China, this oil is used by the river men to impregnate the wood of boats and rafts in order to make them waterproof, hence the name, "China wood oil." This oil has gained a tremendous importance in varnish making; it dries in one-third the time which linseed oil requires, and has other valuable properties of its own, for example, excellent resistance to sunlight. Chinawood oil consists chiefly of the glyceride of elaeostearic acid. Some years ago cultivation of tung trees was started in some of the southern states and the annual U. S. production of tung oil is now about 10,000,000 pounds. The main source of supply is still China, however.

Animal Oils and Fats

Whale Oil. Whale oil formerly was an important source of oil for burning; the advent of petroleum products has relegated it to an unimportant position. The annual world's production of whale oil is about the amount of olive oil imported into the United States. The seats of the whaling industry are Norway, Iceland, and the American Pacific coast.[13]

A large whale yields between 100 and 180 barrels of oil; the blubber or fat is rendered either on board the boat or in the home port. The fat is

[11] *Chem. Industries*, 62, 244 (1948).
[12] *Chem. Industries*, 62, 244 (1948).
[13] There are 4 shore stations, each handling whales caught within a radius of 150 miles: Moss Landing, Trinidad, in California; Bay City, Washington; Akutan, Alaska. Production in 1930, 10 million pounds. The most important whaling grounds of the world today are in the Antarctics, particularly near Ross Sea. (From the Bureau of Fisheries, Department of Commerce, Washington, D. C., and Bureau of Census.)

chopped fine and rendered by heating first by itself, then with water; certain parts of the carcass may also be digested for oil. The uses are for leather dressing, burning oil, soap, and, mixed with mineral oil, for a lubricant. Whale oil is also hydrogenated to a fat.

Fish Oil. Fish oil is obtained by boiling either the whole fish or selected parts in water and collecting the oil which rises. The menhaden, herring, and certain salmons are used in large numbers for this purpose, and many other fish in smaller numbers. The residue in the rendering pots is dried and sold for fertilizer. Fish oil is used in cheap paints to replace part of the linseed oil and for other minor purposes. The oil may be hydrogenated to a fat, at the same time losing its unpleasant odor; such fats are suitable for soap making.

Cod-liver Oil. The cods are brought alive to the home station in steam trawlers, opened, and the fresh livers heated in steam-jacketed kettles. The first oil is prized for its vitamin A and D content, and is used for medicinal purposes. On continued heating a second grade of oil is obtained, which is used in fine poultry raising. Livers which are brought in partly decomposed are rendered for an oil used in the dressing of leather. The livers of many other fish are similarly treated, the most important being halibut, tuna, and shark.

Lard and Lard Oil. The fat of the pig is rendered by heating it with water in closed, cast-iron vessels under pressure and provided with an outlet for the release of overpressure caused by the formation of gases. After digesting, the liquid is run off; by cooling it moderately, a division into the liquid part, the lard oil, and into a solid part, the lard proper, is made.

The operation of rendering has recently been improved and accelerated. In the circulating rendering process of Wurster and Sanger, Chicago, several desirable ends have been reached: (1) quick heating, which reduces the time factor and the objectionable yellow color; (2) low temperature, avoiding scorching; (3) larger capacity for a given time period.

The equipment for this process includes a tubular heating element with vertical tubes through which the ground material passes, flash chamber, a circulating pump, separator, and a vacuum pump. The tubes are heated by exhaust steam, under 5 pounds pressure. The material is drawn from the base of the tubes by a centrifugal pump of the non-clogging type, and is returned at a point just above the tubes. The heater is surmounted by a flash chamber in which the gases evolved are collected before they pass to a separator where the droplets of entrained fat are recovered, to be returned to the main drum. From the separator, the gases go to the steam ejector, which maintains a low pressure on the system. After the material is completely melted, it is discharged into a settling tank, from which the clear fat is drawn off. The sediment, called cracklings, is run to a filter press.

With a heating surface of 1000 square feet, a charge of eight tons is rendered in two hours. Compared with the older type of jacketed melters using high pressure steam (50 pounds), it is found that the new rendering process equipment works four times as fast, besides producing a paler product. Several other details are exhibited in Figure 225.

Tallow. By tallow is usually meant beef tallow, which is rendered in the same way as lard. There is also a mutton tallow, a sheep tallow, and others. Their chief use is for soap-making.[14]

Butter. The cream in cow's milk isolated in a centrifugal separator is rich in small globules of fat, which coalesce on churning; the lump so formed, after addition of salt (in the U. S.), is table butter; it is about 83 per cent butter fat, the rest water and salt.

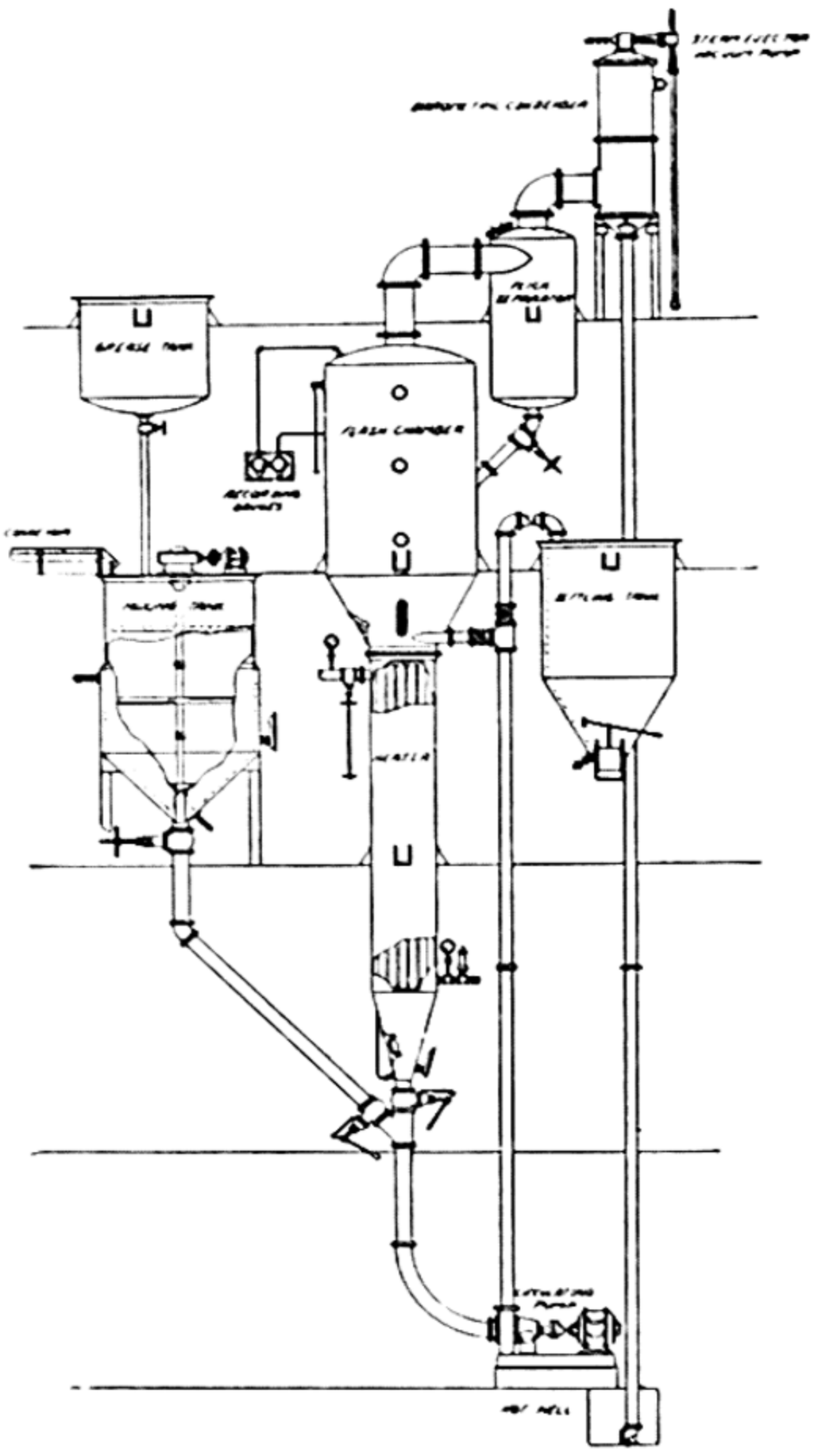


FIGURE 225.—A circulating rendering plant. (Courtesy of Wurster and Sanger, Inc., Chicago.)

Oleomargarine [15] is a widely used composite food manufactured according to several recipes. The following is an example: a "fat blend" consisting of hydrogenated oils, 80 per cent; skim milk moisture, 16 per cent; salt, 2.75 per cent and milk solids, 1.25 per cent; vitamin A, a preservative (usually sodium benzoate) and artificial flavor (diacetyl and acetylmethylcarbinol). In the churning process, the fat blend and the aqueous liquid are emulsified. The production of oleomargarine in the United States in 1947, as shown in Table 111, was 715,500,000 pounds; the production of butter was

[14] Lard m.p. 36° to 40° C.; tallow, 40° to 45° C.

[15] "A bread spread made him famous," brief story of the invention of the original margarine, by Mège-Mouries, *Oilways*, p. 21, April, 1948, "The manufacture of margarine," A. J. Andersen, *Trans. Inst. Chem. Eng. (London)*, *22*, 1 (1944); the same article in *Ind. Chemist (London)*, 20, 82 (1944).

1,626,000,000 pounds. The production, sale, and coloring of margarine are subject to Federal and State legislation.

Waxes

Sperm Oil. Sperm oil is obtained principally from the content of a cavity in the head of the cachalot or sperm-whale. When the oil is cooled it deposits a solid wax, the spermaceti, used in pharmacy and in candlemaking. The oil under the name of sperm oil is valued as a lubricant for light, high-speed machinery; like rape oil, it has no gumming tendency. The chief ester in spermaceti is cetyl palmitate, $C_{16}H_{33}O \cdot OC \cdot C_{15}H_{31}$. Cetyl alcohol is a monohydric alcohol $C_{16}H_{33}OH$. Sperm oil similarly contains alcohols combined with fatty acids different from glycerin (annual production about 1 million pounds).

Carnauba Wax. Carnauba wax is found on the leaves of a palm tree in Brazil, the *copernicia cerifera*. The leaves are gathered and rubbed to dislodge the coating: it is purified by melting, decanting from the deposit, and cooling. It has a high melting point, 105° C., and is used in the varnish industry and in furniture and shoe polishes and in carbon paper coating. It is the hardest wax known.

Beeswax. Beeswax is obtained from the honeycomb of the common bee; it is purified by washing and bleaching. Industrially, it is of small importance, though it is used in large quantities in the manufacture of church candles, many of which contain over 50 per cent beeswax.[16]

Waxes are esters of monohydric alcohols—in a few instances, of dihydric alcohols—as contrasted with fats, which are esters of the trihydric alcohol glycerol (or glycerin). The interest in waxes at times arises from interest in the alcohol they contain. Wool wax has been studied, in part for its alcohol.[17]

Hydrogenation

The hydrogenation of oils with the aid of a catalyst is an important industry. The reaction is used mainly for the hardening of vegetable oils to edible fats; in the United States, cottonseed-oil hardening was first developed. Now not only vegetable but fish oils are hardened to products some of which are edible and some suitable only for stock for soap manufacture and fatty acid preparation.

The procedure is to suspend finely divided nickel in the oil heated to 250 to 300° F. (121 to 149° C.), and pump in hydrogen gas. The reactor is a tall, cylindrical vessel almost filled with the oil mix, provided with a circulating pump which takes the oil at the bottom and returns it, for the main part, at the top. The part not returned is the product, which leaves by a branch line. The reactor or hydrogenator may have mechanical agitation by a turbine-type (or other) agitator with a vertical shaft, entering from the top, or a propeller agitator entering at the side, below the liquid (best); or the agitation may be provided by a perforated pipe distributor at the base of the vessel. The returned liquid is generally sprayed in. The nickel is

[16] Some other waxes of interest to the perfume maker are discussed in Chapter 30.
[17] "Wool wax alcohols, Part 1," E. S. Lower, *Ind. Chemist (London)*, 20, 319 (1944).

used in amounts 0.5 to 1 per cent of the oil; it may be introduced in the form of the oxide, which is soon reduced to the metal by the gas, or in the form of Raney nickel, obtained by treating a pulverized alloy of nickel and silicon (60 to 40, or 50 to 50), with caustic solution.[18] The finished product is filtered and stored warm, as a liquid; the filtered catalyst is mixed with fresh oil and used over again. Palladium is a more effective catalyst than nickel; 1 part in 100,000 parts of oil is sufficient, and the reaction proceeds at a lower temperature and in less time. It is rarely used, however, because of its high cost. The catalyst may be supported on some inert medium such as diatomaceous earth.

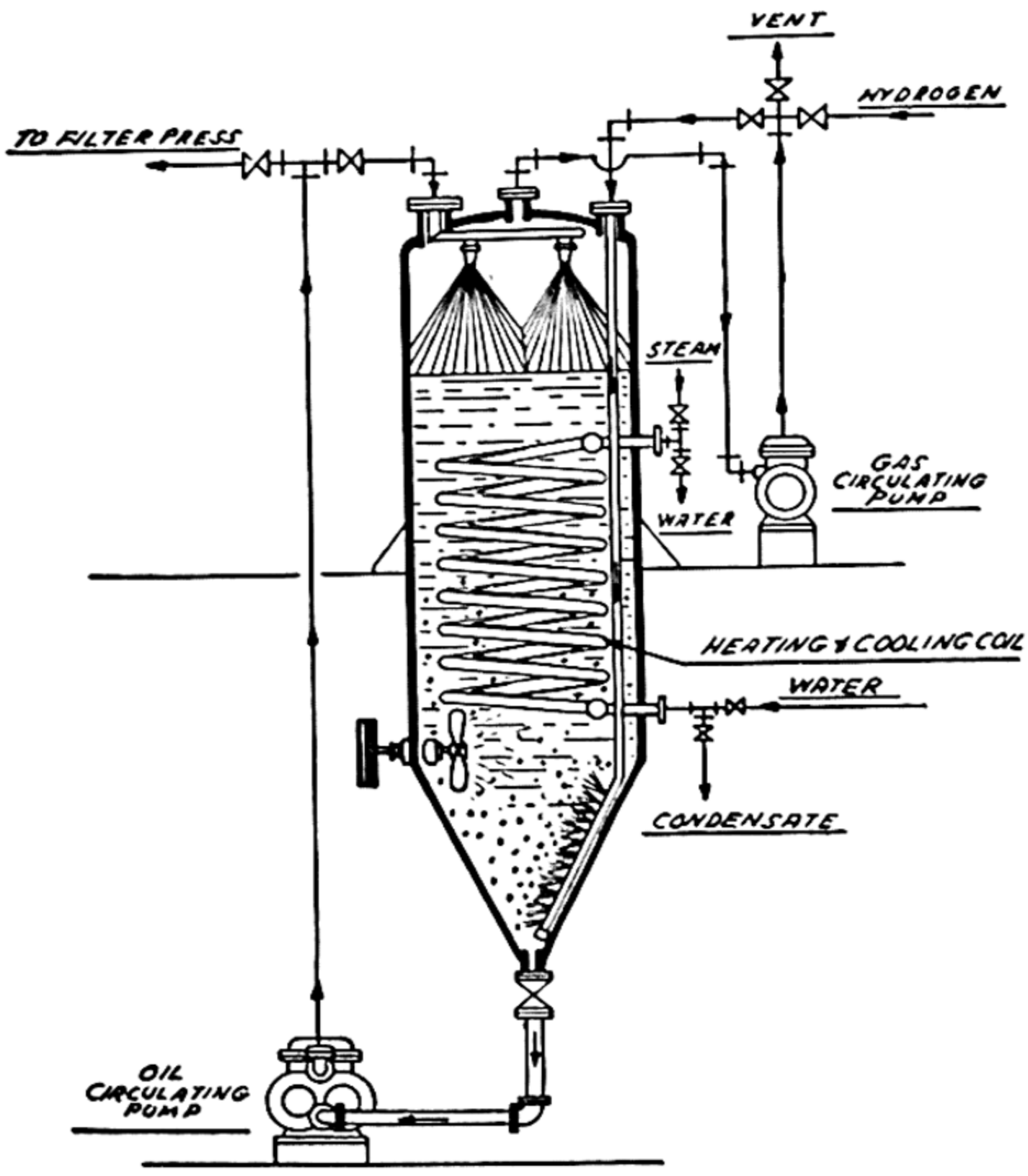


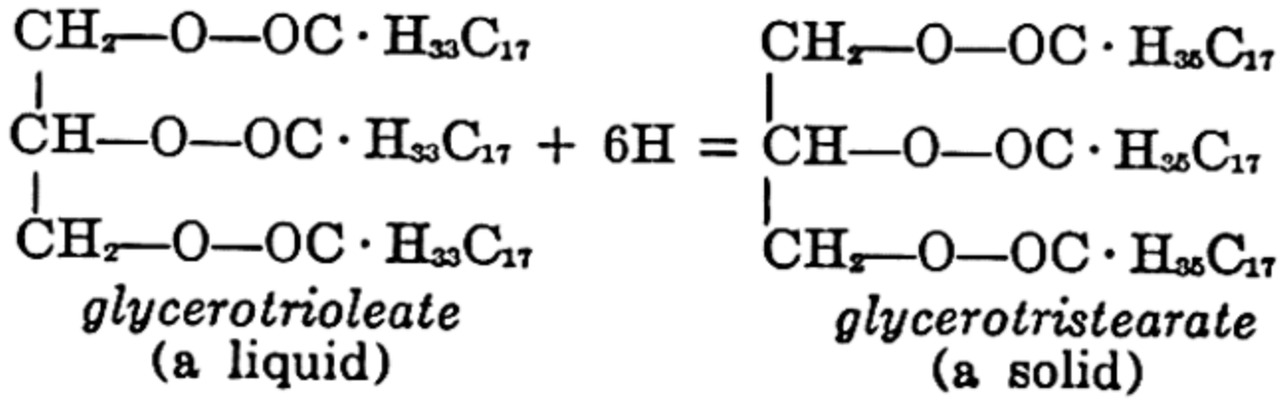
FIGURE 225a.—Hydrogenator for vegetable oils with inside heating and cooling coil, oil and catalyst circulating pump, gas circulating pump, and propeller-type mechanical agitator below the liquid line. The new oil enters at oil pump; entry not shown. [*Ind. Eng. Chem.*, 32, 1196 (1940).] (By permission.)

The hydrogenation reaction is exothermic for all oils, so that after the reaction is started, some of the oil circulated must be cooled by passing it through an outside cooler. The product is removed after the hydrogenation has proceeded to the desired point, which is conveniently determined by following its progress with a refractometer; it is cooled somewhat, and if desired, it is deodorized by passing carbon dioxide into the melted fat heated to 130° C. (266° F.) for an hour, or by some other method. On cooling it is a soft solid, a semi-synthetic fat. It has been found advisable to hydrogenate until the desired melting point is reached and then to stop, rather than to hydrogenate to the limit, and rely on mixing with fresh oil to attain the desired melting point. If completely hydrogenated, cottonseed oil

[18] U. S. Pat. 1,563,587; 1,628,190; 1,915,473.

would melt at 62° C. (143° F.). To be edible, a fat should melt below body temperature.

Among the oils, any glyceride which is unsaturated may be hydrogenated; for example, glycerotrioleate, a liquid, is thus changed to glycerotristearate, a solid.



glycerotrioleate (a liquid) — *glycerotristearate* (a solid)

Reading References

"Fats: the component glycerides of a mutton tallow," G. Collin, T. P. Hilditch and C. H. Lea, *J. Soc. Chem. Ind.*, 48, 46T (1929).

"Hydrogenation in practice and theory and the manufacture of hydrogen," E. F. Armstrong, *Trans. Inst. Chem. Eng. (London)*, 9, 139-157 (1931).

"Vegetable fats and oils," George S. Jamieson, Second Edition, Reinhold Pub. Corp., New York, 1943.

"Edible oils and fats," C. Ainsworth Mitchell, New York and London, Longmans, Green and Co., 1918.

"Linseed oil and other seed oils," W. D. Ennis, New York, D. Van Nostrand Co., 1919.

"Hydrogenation of organic substances, including fats and fuels," Carleton Ellis, New York, D. Van Nostrand Co., 1930, 3rd ed.

"The chemistry of drying oils," R. S. Morell and H. R. Wood, New York, D. Van Nostrand Co., 1925.

"Some remarks about oiticica oil," Dr. Otto Eisenschiml and Gerald Eisenschiml, *Paint and Varnish Prod. Mangr.*, 14, No. 5, 18 (1937).

"Hydrogenation of fats," Oscar H. Wurster, *Ind. Eng. Chem.*, 32, 1193 (1940).

"The manufacture of margarine," A. J. Andersen, *Tr. Inst. Chem. Eng. (London)*, 22, 1 (1944).

"The solvent extraction of soybean flakes," Charles O. King, Donald L. Katz, John C. Brier, *Tr. Amer. Inst. Chem. Eng.*, 40, 533 (1944).

"Solvent extraction of vegetable oils," S. E. Tray and C. W. Bilbe, *Chem. Eng.*, p. 139, (May, 1947).

"Drying oils," George M. Sutheim, *Chemical Industries*, 62, Part I, p. 65; Part II, p. 241 (1948).

"Adventures in Man's First Plastic: the Romance of Waxes," by Nelson S. Knaggs, Reinhold Pub. Corp., New York, 1947.

Formerly the materials used by the perfume maker were entirely natural products; these are now supplemented by a number of synthetic products. The preparation of the synthetic substances and improved methods for the extraction of natural substances are the contributions of chemical science to the perfume industry. The work of the perfume maker, which consists of the proper blending of odoriferous substances, requires artistic sensitivity as well as scientific knowledge.

Chapter 30

Essential Oils, Perfume Sundries, Flavors;* Pharmaceuticals, Antibiotics†

Part I. Essential Oils, Perfume Sundries, Flavors

Perfumes are made from essential oils, the odoriferous principle of a number of plants. Usually a number of oils are blended together, in alcohol solution, and a fixative is added in order to render more lasting the odor which otherwise would be fugitive. A perfume may therefore be said to consist of three parts: the odoriferous part, the fixative part, and the diluent.

Table 112.—*Essential oils, with place of origin.*

Oil lavender fleur	from the flower, hence "flower oil"	France
Oil ylang ylang Bourbon†	from the flower	Réunion
Oil of rose	" " "	Bulgaria and France
Oil of patchouli	from the leaf	Singapore
Oil eucalyptus	" " "	Spain and Australia
Oil geranium	from the herb	Bourbon Islands, Algeria and France
Oil rosemary	" " "	Spain and France
Oil thyme red	" " "	Spain, France and Syria
Oil bergamot	from the fruit	So. Italy
Oil orange and oil lemon	" " "	So. Italy, California, West Indies, Africa, Florida and Brazil
Oil fennel	from the seed	Middle Europe
Oil anise	" " "	China, Spain, Russia
Oil caraway	" " "	Europe, North Africa
Oil bois de rose	from the wood	French Guiana and Brazil
Oil guaiac wood	" " "	Paraguay+Argentine
Oil vetivert	from the root	Bourbon Island, Java and Haiti
Oil of orris (a solid)	" " "	No. Italy and So. France
Oil olibanum	from the gum	Arabia, Levant
Oil cinnamon Ceylon	from the bark	Ceylon
Oil citronelle Java	from the grass	Java
Oil palmarosa (Turkish Geranium)	" " "	India

† Old name for the French possession Réunion.

The function of the diluent, practically always ethyl alcohol, is to reduce the concentration of the blended oils to an odor strength similar to that of the flower. The number of typical fixatives is small; the numbers of essen-

* In collaboration with Mr. Earl Booth, chemist-perfumer, Larkin Company, Buffalo, N. Y.

† Reviewed by Dr. J. B. Sprowls, Professor of Pharmacy, Temple University, Philadelphia.

tial oils, very large. The synthetic substances are usually pure chemical substances, whereas the essential oils are natural mixtures. Some synthetics are artificial reproductions of natural substances, others give entirely new odors.

Essential oils are obtained not only from the flower, but also from the leaves, roots, and seeds of plants, and from the roots and barks of trees. Table 112 gives a number of examples, with the places of origin.

Essential oils are used not only for perfumes proper, but also for perfuming soaps; for that purpose they must be lower in cost. As a rule an essential oil costing less than $5 a pound may be used for soaps. For perfumes proper, there is no price limit, except that for the less expensive perfumes, the cheaper raw materials must be used; many of these are synthetics. Examples of synthetics follow:

Class	*Samples*
acids	Benzoic acid, Phenyl acetic acid (solids)
alcohols	Linalool, Terpineol (liquids)
aldehydes	Benzaldehyde, Phenyl acetic aldehyde (liquids)
esters	Amyl salicylate, Benzyl acetate (liquids)
ether	Di-phenyl oxide (solid)
ketone	Ionone α and β (liquids)

Among the synthetics, certain ones are made from benzene, toluene, phenol, or other coal-tar products; thus benzoic acid and benzaldehyde from toluene, diphenyl oxide from phenol. These may be said to be true synthetics. Others are semi-synthetic only, for they are made from a natural plant product; thus ionone is made from citral, which is isolated from lemon-grass oil. If a constituent of a natural oil is isolated, by distillation for instance, and used as such, it is called an isolate; thus geraniol is an isolate from citronella oil.

A number of essential oils are used as flavors as well as perfumes, for instance the oils of lemon, limes, and orange (peel). Vanillin, oil angelica, and coriander oil are used both for flavoring and for perfumes. Another example is oil of peppermint which has a further interest in that on cooling it,[1] large crystals of menthol separate. Oil of peppermint, chiefly the domestic oil (*Menthae piperita*), is much used in dental pastes as a flavor, and also as a pharmaceutical. Formerly the pharmaceuticals were chiefly plant extracts; now they include a large group of manufactured chemicals, of constantly increasing number and importance.

Essential Oils

Essential oils are obtained by extraction with volatile solvents, by steam distillation, by expression, and by enfleurage.

Extraction by means of volatile solvents is of wide application, and is the most important method for fine oils. The practice in southern France for oil of rose may serve as example. The rose cultivated in Provence is chiefly *Rosa centifolia*, a pink rose. The petals are placed on trays in copper vessels and percolated with low-boiling petroleum ether; the waxes

[1] Japanese peppermint oil, *Menthae arvensis*, is rich in menthol.

present are dissolved as well as the oil. The solvent is removed in stills under reduced pressure so that only very gentle heat is required, and there is left a semi-solid residue, called concrete, and containing about half its weight of oil. The rose concrete is next dissolved in warm alcohol, and this solution is cooled. The waxes separate and may be removed by filtration. The filtrate is placed in small copper stills, the alcohol removed by distillation, and there is left the pure oil of rose, called rose absolute No. 1. The waxes may be washed again, giving a solution called rose extract. The amount of oil in one rose blossom is very small; to produce 1 ounce of rose absolute, some 60,000 blossoms are required. By weight the yield is about 0.1 per cent. The price is about $10 an ounce, and this is not too dear considering the labor involved in growing and preparing the many blossoms required.

The best known concretes are rose, jasmin, tuberose, orange flower, cassie (a small yellow flower), and lavender; the corresponding absolute oils are made by alcoholic extraction. Concrete violette de Parme, formerly so well known, is now extinct in perfumery. Some perfumers prefer to buy the concrete, and make their own alcoholic extracts of the same without reducing it to the absolute form.

The most expensive of the absolute oils is violet, which brings $75 an ounce if free from any addition. Violette de Parme is almost too dear for the odor value received when compared with modern ionones, and for that reason, violet perfumes are made chiefly from methyl ionone, a semi-synthetic.

In order to obtain the oil by distillation, the blossom, herb, or chipped root is placed with water in a still with goose-neck, and heated by a steam coil, or steam jacket, or by live steam introduced below the false bottom on which the material rests. For peppermint. which is a good example, the distillate may be cooled in a condenser made of ordinary conductor pipes such as are used for rain drainage on dwellings; the cooling is by cold water. The first home-made installation has been replaced in most cases by modern equipment. In the receiver, two layers form, the oil being the upper one; the water layer is wasted, in this case. In the case of rose blossoms, however, the water retains a certain amount of oil in solution, and is then carefully preserved and sold as such, for the demand is considerable. The proportion of rose water to oil may be reduced if desired by returning it to the still so that new water need not be introduced; in such cases a steam jacket would be the source of heat. Bulgarian otto of rose is a distillation product and is the ordinary otto of commerce; real French otto of rose is rarely seen at the present time because the production cost is less in Bulgaria. The blossoms used in Bulgaria are the *Rosa Damascena,* a red rose.

There may be a combination of odors in the distillation itself with good results; thus geranium (the whole plant) may be distilled by itself, giving geranium oil; or rose petals may be added to geranium oil made the previous fall, and the two distilled together, with the production of oil of geranium sur roses, possessing a superior odor.

Steam distillation is suitable for the production of the oil because the

essential oils are either insoluble, or very slightly soluble in water. The industry is seasonal, so that every year the raiser of peppermint or spearmint uses the still for two or three weeks; a simple installation is economically correct. For many oils, the dried leaves or roots, produced in one place, may be shipped to a center for extraction, and in that way material provided for constant operation; in such centers very elaborate machinery may be provided. The most important of these centers is Grasse, near Nice; it is surrounded by flower-producing areas, and in addition receives imported materials such as patchouli leaves and vetivert roots from the East Indies and India, and orris root from Italy (Florence). The important products at Grasse are neroli oil from the bitter orange blossom, jasmin, verbena, narcissus, jonquil, orris, tuberose, cassie, and violet; these are not excelled by products produced elsewhere. French lavender oil is the main lavender oil; English lavender oil formerly was of importance, but is now practically extinct. Material reaching the market labeled English lavender oil is usually a blend of French oils. Steam distillation is the chief method of producing oils, thus, orange blossom, verbena, orris and lavender; the second method is extraction by volatile solvents, already mentioned.

Other products of steam distillation are oil of cloves, cinnamon oil from the bark (very little), coriander from the crushed seed, guaiac from the wood, found in Argentina, oil bois de rose, which has no relation to the rose blossom or its oil but is obtained from a laurel in French Guiana; oil vetivert; citronella oil from Java (best) and Ceylon; and geranium oils.

The peel of the orange, the bergamot, a small citrus fruit on the order of the lime, and the lemon, are pressed, both by hand and by machinery, in order to obtain the oil they contain; there is also a distilled oil of these peels, of inferior value. The oils have a high content of terpenes and stearoptene (stearoptene is the name given to any wax which separates from an oil on standing). In order to concentrate the citral, the characteristic odoriferous part in the case of lemon oil, the terpenes are removed by distillation in a steam-jacketed vacuum still (not by directly introduced steam), and the residual oil is then terpeneless oil of lemon, or orange. The distillate serves as diluent for inferior quality or synthetic oils. It is because of the high terpene content (about two-thirds) of these oils that the odor changes on standing. Presumably the terpenes polymerize, gaining in odor, until the odor of the citral is overbalanced; the spoiled oil is termed rancid. Chemically pure citral is mentioned in the next division.

In enfleurage by the cold process, the flower or the separate petals is pressed against warm fat, a fine grade of benzoinated lard, spread on glass plates 1 foot wide by 2 feet long, fitted with wooden frames. Both sides of the glass are greased; petals are placed on the upper side only, and the frames piled on one another, so that the lower side touches the petals on the glass of the frame below. After a day the petals are removed by hand, or by a brush, fresh petals spread on, and this repeated until the lard has the maximum amount of oil it can absorb. The lard is then scraped into containers and preserved in cooled cellars; at this stage the product is pomade, formerly used as such. From the pomade, the absolute oil is

obtained by extraction with alcohol, followed by a distillation to remove the solvent, and in order to distinguish such absolute from that obtained by the volatile solvent method, it is called "absolute pomade," thus Jasmin Absolute Pomade. This process is used less than formerly; much labor is involved, and the fat tends to turn rancid; efforts to substitute soft paraffin waxes have not been successful, because their absorption power is low. A modification of enfleurage is to macerate the rose blossoms with warm fat, filter from the blossoms, and cool; the resulting pomade may be extracted for the oil by alcohol. The alcohol is recovered. Rose and orange blossom pomades are made by the hot process, jasmin and tuberose pomades by the cold enfleurage process.

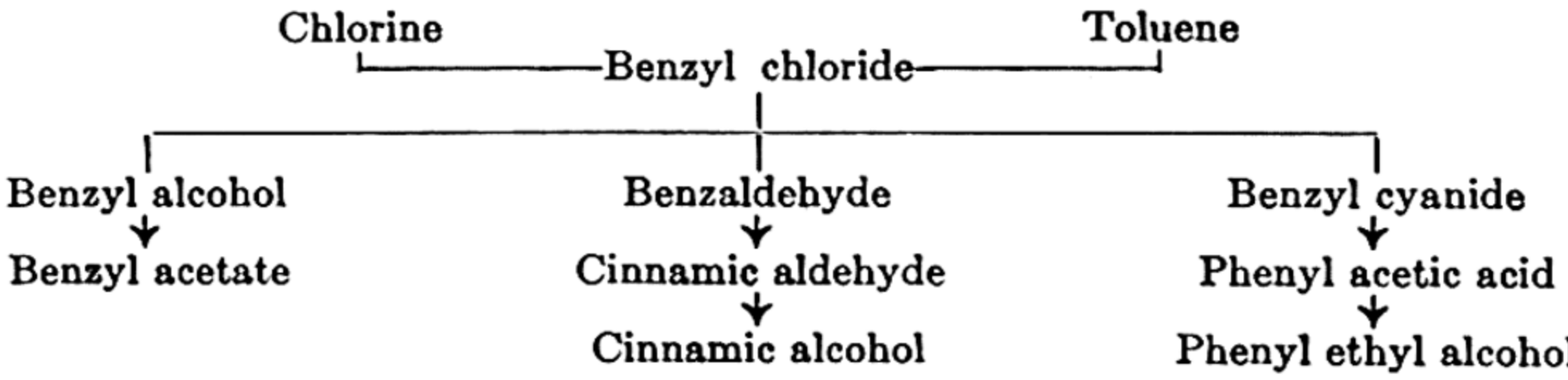
TABLE 113.—*Approximate annual production of essential oils.*

Otto of Rose	3600 kilos to 1000 kilos (varying according to seasons)
Oil Lemon It.	1,200,000 lbs.
Oil Orange It.	250,000 lbs.
Oil Orange Sp.	70,000 lbs.
Oil Bergamot	400,000 lbs.
Oil Aspic Lavender Sp.	220,000 lbs.
Oil Rosemary Sp.	330,000 lbs.
Oil Lavender Fr.	300,000 lbs.

SYNTHETICS, SEMI-SYNTHETICS, AND ISOLATES

Benzaldehyde is made by chlorinating toluene, and boiling with caustic; its odor is similar to that of bitter almond oil. Nitrobenzene [2] is called oil of mirbane, and has a penetrating odor; its use is chiefly for soaps and for shoe polish. Dimethyl hydroquinone is a white solid, valuable for synthetic narcissus perfumes. Cinnamic aldehyde has been sold under the name of Cassia oil redistilled; it may indeed be isolated from cassia, but like the other substances in this paragraph, it is made synthetically with great ease and at low cost.

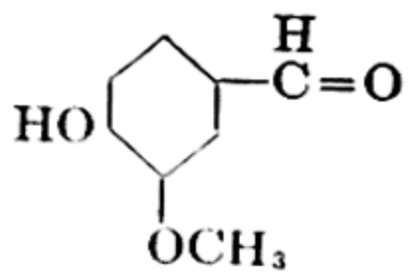
The chemical relation between a number of synthetics is shown below:



Vanillin [3] is a semi-synthetic; it is made (1) from iso-eugenol which itself is made from eugenol, an isolate from oil of cloves or cinnamon leaf

[2] Chapter 27.

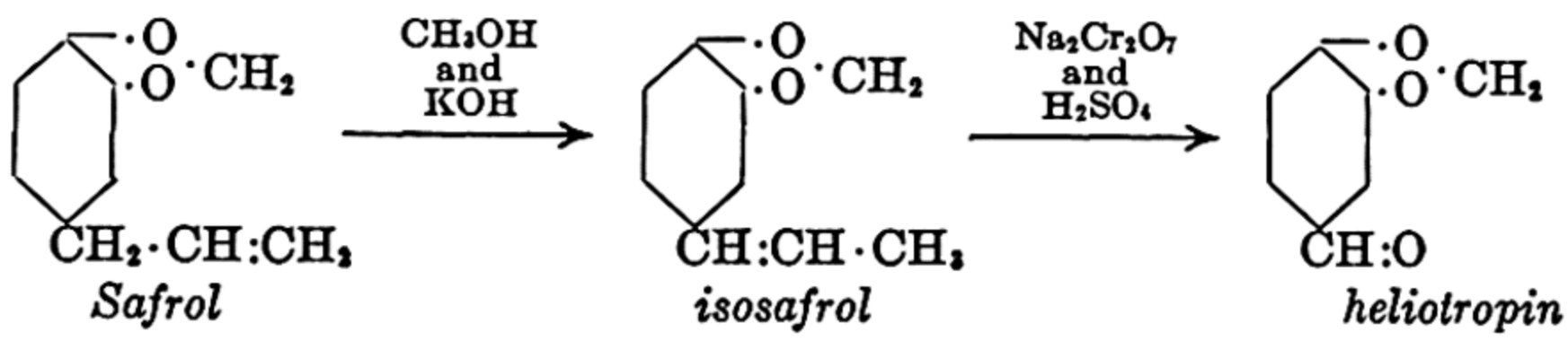
[3] Vanillin (solid)



oil; (2) from guaiacol fractionated from the phenols in coal-tar; (3) from wood pulp. Vanillin is a white solid, and in this form is used by the perfumer, rather than in the form of the extract from the vanilla bean. The odor of vanillin is delicate; vanillin forms part of a surprisingly large number of perfume formulas. Piperonal is a solid aldehyde, sold under the name of heliotropin, and made by the following scheme of transformations:

Camphor oil (Formosa and Japan)

Camphor — Safrol

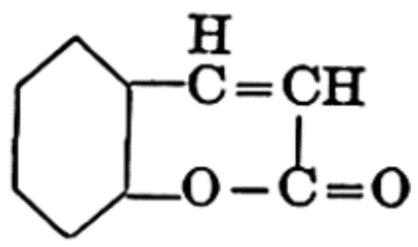


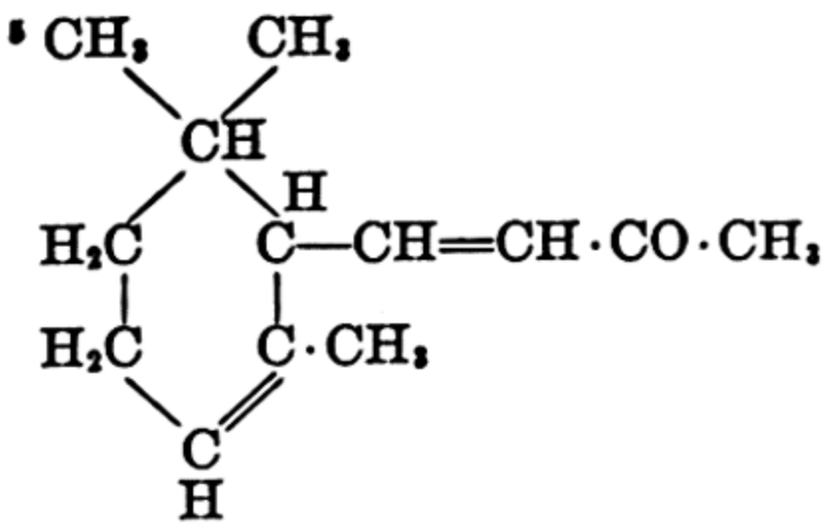
Safrol — *isosafrol* — *heliotropin*

Coumarin [4] is made synthetically, from salicylic aldehyde, although it occurs naturally, for instance in tonka beans; it is a white solid prepared from salicyl aldehyde; its odor is sharper and more penetrating than that of vanilla. The most remarkable of the semi-synthetics are the ionones,[5] two ketone isomers differing only in the position of a double bond (unsaturation); α-ionone is about \$8 a pound, β-ionone about \$6. The ionones are made by condensing citral with acetone, and boiling with dilute sulfuric acid. Citral is a liquid of formula $(CH_3)_2 \cdot C : CH \cdot CH_2 \cdot CH \cdot C(CH_3) : CH \cdot CHO$, and is isolated from lemon-grass oil by forming the sodium bisulfite addition compound; pure citral is \$2 a pound. The two isomeric ionones are separated by their sodium bisulfite compounds, which differ in solubility (the α-ionone compound is less soluble). Methyl ionone with suitable admixtures produces a true violet odor. All the substances in this paragraph except coumarin are semi-synthetics.

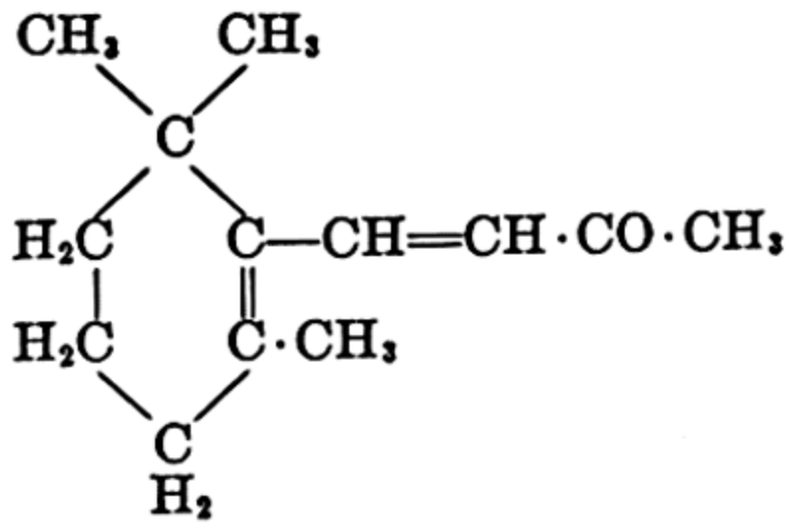
Geraniol is an important substance, an example of an isolate; it is obtained from palmarosa oil or citronella oil, and serves to imitate the rose odor.

Coumarin (solid)

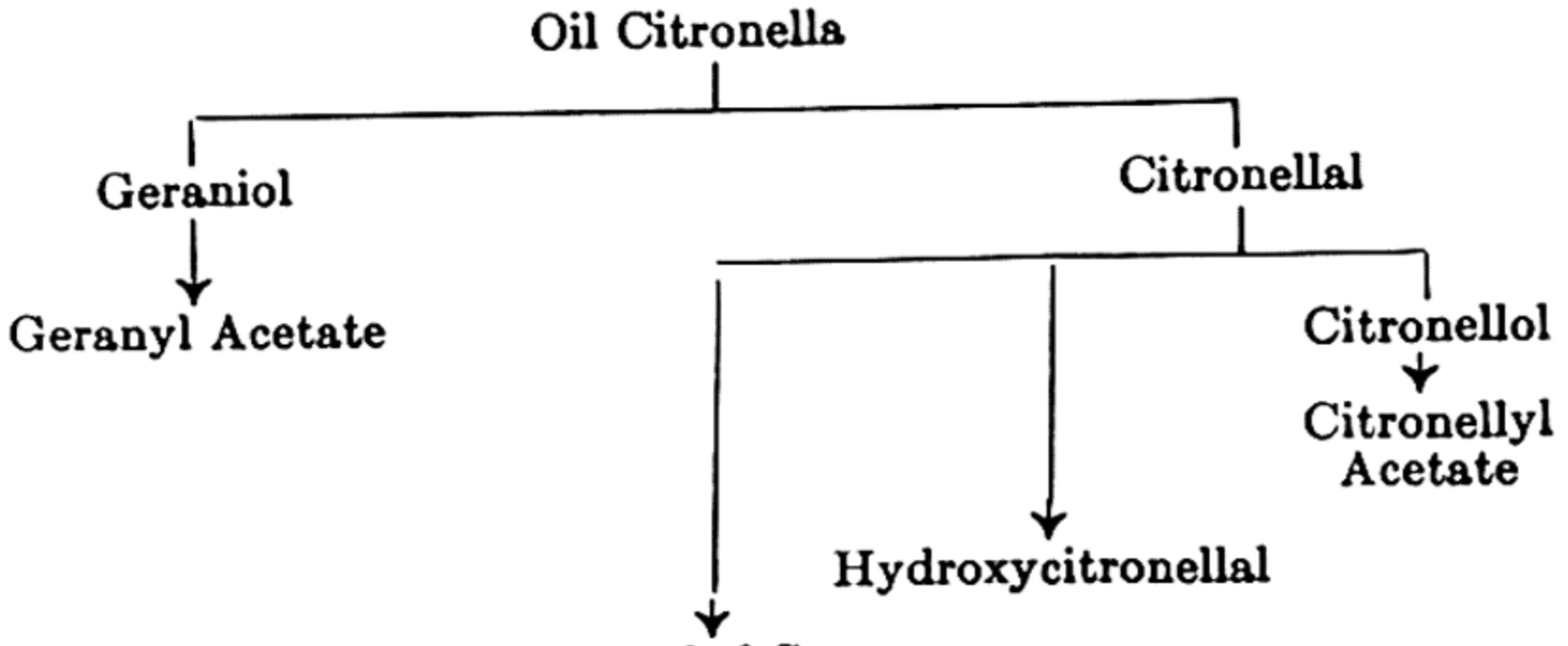




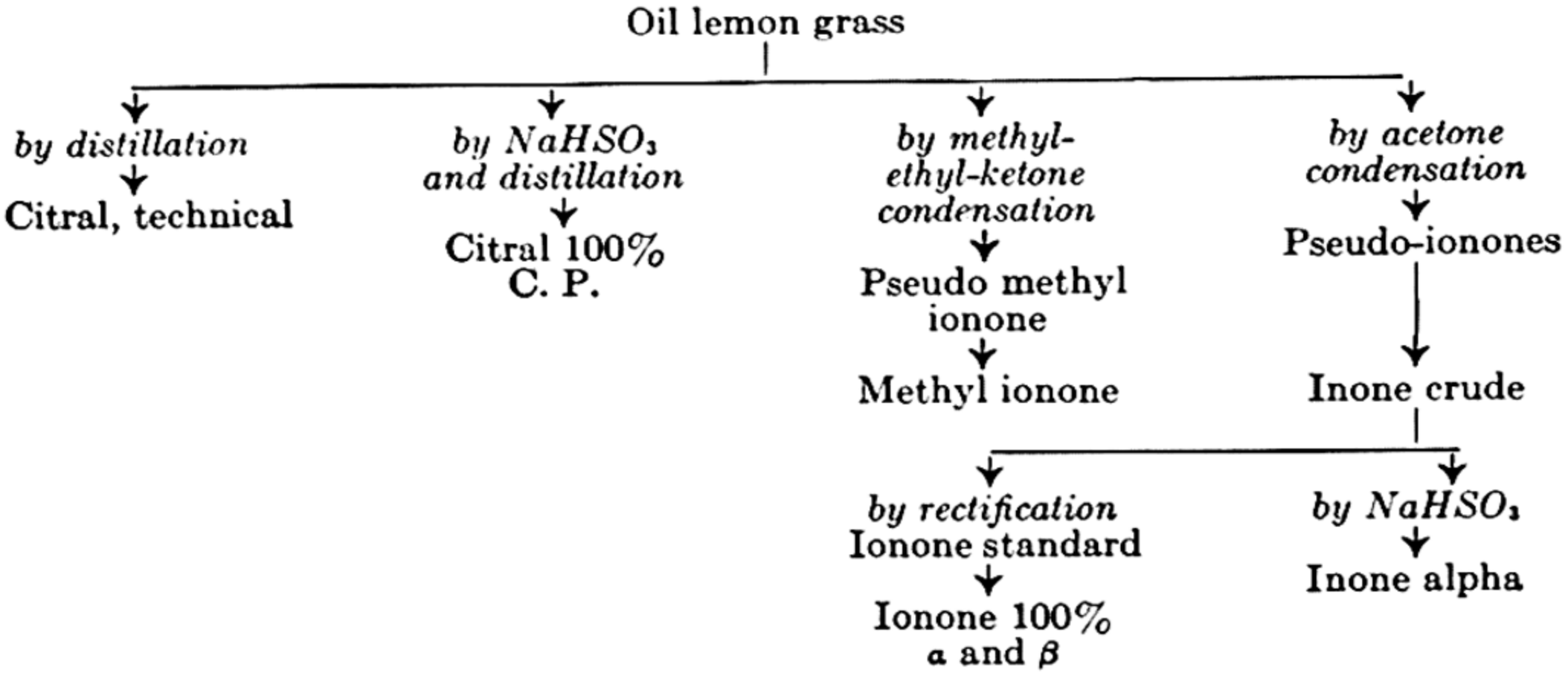
α-ionone (liquid)



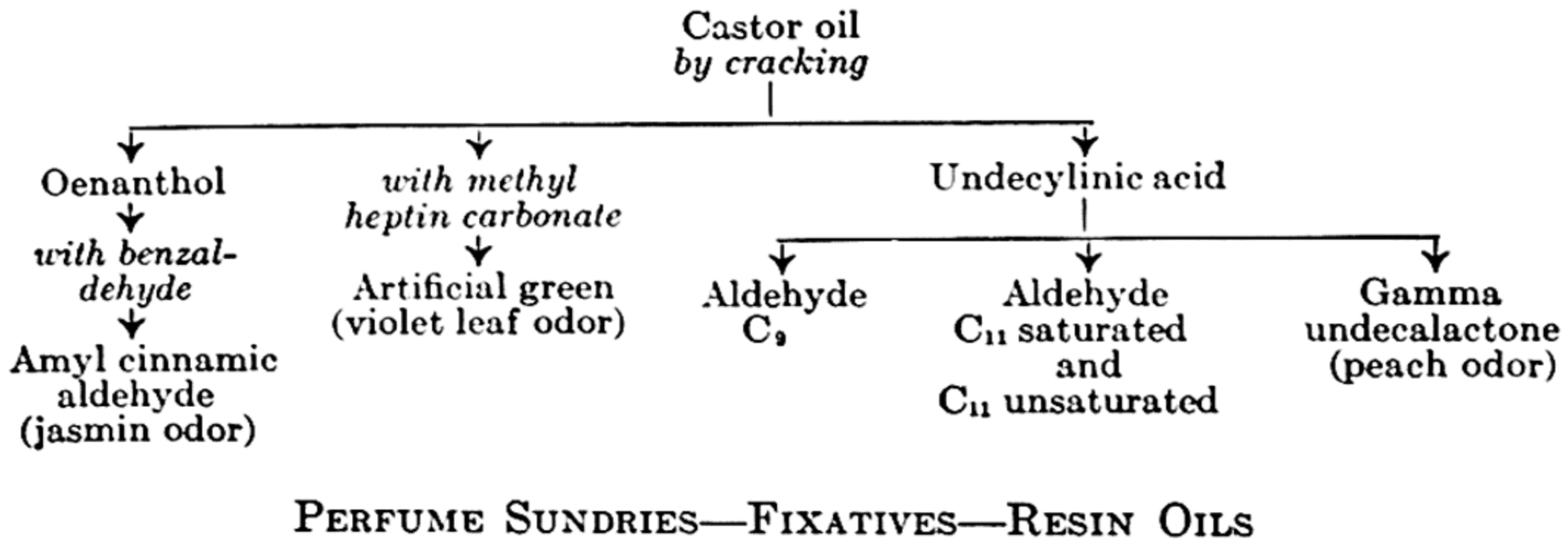
β-ionone (liquid)



From lemon-grass oil, a number of valuable semi-synthetics are obtained:



A new method of preparing a number of semi-synthetics for their odor and flavor is the cracking of castor oil, with subsequent treatment of the cracked distillate.[6]



Perfume Sundries—Fixatives—Resin Oils

Under perfume sundries any substance is included which enters into a formula for a perfume without directly contributing to its odor. The fixative serves primarily to render the odor more lasting; it is chosen so that it blends well with the oil odor. Three substances have been used for many years past and are still the most important fixatives; these are ambergris, musk, and civet.

[6] For definition of cracking *compare* the chapter on petroleum.

Ambergris is a calculus in the stomach of the sperm whale which has formed around a sharp foreign substance such as the beak of the squid, and which is excreted and found washed ashore; it may be also cut from the stomach of a whale caught for its oil. Ambergris is dissolved in alcohol, and used in tincture form. Its odor is earthly, and its fixative power remarkably great; it is used for the floral perfumes.

Musk is the dried secretion from the preputial follicle of the musk deer, found in Tibet and in Manchuria; it has not been possible to raise the deer in captivity. The musk pod is situated at the stomach of the deer; each pod yields about an ounce of musk, worth about $22. The odor of crude musk is disagreeable, but the alcoholic solution after aging several months is not unpleasant. Musk is the fixative for the so-called oriental perfumes (heavy perfumes).

Civet is obtained from the civet cat, in Abyssinia; crude it is also disagreeable; in the form of aged alcoholic solution, it is used as musk is. Frequently both musk and civet are used in one perfume.

Artificial musk is a synthetic product, which has fixative value; the first was musk xylene; the best one at present is musk ambrette, dinitro-butyl-metacresol-methylether, made from cresol. Among the essential oils, vetivert, orris, and some others sometimes perform the function of fixatives.

Odoriferous resin oils and oleo-resins are important mainly for their odor, only secondary as fixatives. Oleo-resin of olibanum is made from a gum-resin obtained by incisions in the bark of pine growing in the Levant (Asia Minor), the *Boswellia Carterii.* The gum-resin is extracted with alcohol and filtered from the non-solubles (gums); the alcohol of the solution is distilled and there is left a viscous mass, the oleo-resin, with the odor of church incense. By distilling the gum-resin itself, oil olibanum is obtained. Olibanum is the frankincense of the ancients. Labdanum, found on the leaves and stem of a low plant, yields similarly, oil labdanum. Liquid amber also belongs to this class of fixatives.

Perfumes

Perfumes contain from 2 per cent (weak) to 10 per cent (very strong) odoriferous matter including fixatives; the remainder is alcohol (ethyl). The floral perfumes imitate single flowers, while fancy or bouquet perfumes do not. As example for a simple perfume formula, of the floral type, the following is given:

Type of formula for rose perfume—highest type.

	Grams
Oil of rose (the natural floral oil, the otto)	10
Rose absolute (floral oil, from the concrete)	10
Geraniol (an isolate)	25
Phenylethyl-alcohol (a synthetic)	20
Oil of geranium (an essential oil)	10
Alpha-ionone (semi-synthetic)	15
Resin of labdanum (resin oil)	5
Tincture of musk	5
Alcohol (90%)	900

This would be a strong perfume of fine quality. Examples of fancy perfumes are Chypre and Ambre, both of the oriental type.

Toilet Waters

Toilet waters form a class of perfumes by themselves; they are made up with alcohol chiefly; that they are nevertheless called waters is because the French word for water is frequently used for "liquids."[7] The best-known toilet water is Eau de Cologne; the original formula required a distillation, as indicated in the following one, a close approximation:

Bergamot oil	10 cc.
Lemon oil	15 cc.
Lime oil	5 cc.
Orris root	20 grams
Alcohol (90%)	480 cc.
Water	60 cc.

This is permitted to stand 24 hours, and is then distilled; to 480 cc. of the distillate there are added

Neroli oil bigarade	3.0 cc.
Rosemary oil	0.5 cc.
Lavender oil French	0.5 cc.
Oil of thyme	0.5 cc.

The whole is matured one month. The odor is refreshing, not very lasting. Eau de Cologne is now frequently made without a distillation.

Lavender water is a favorite in England; a simple formula is:

Lavender oil French	20 cc.
Bergamot oil	10 cc.
Sandalwood oil	1 cc.
Civet extract (5%)	5 cc.
Orris resin	4 grams
Alcohol (90%) to make	1000 cc.

Florida water, an American toilet water, contains orange-flower water and cinnamic aldehyde, which give it its distinctive note.

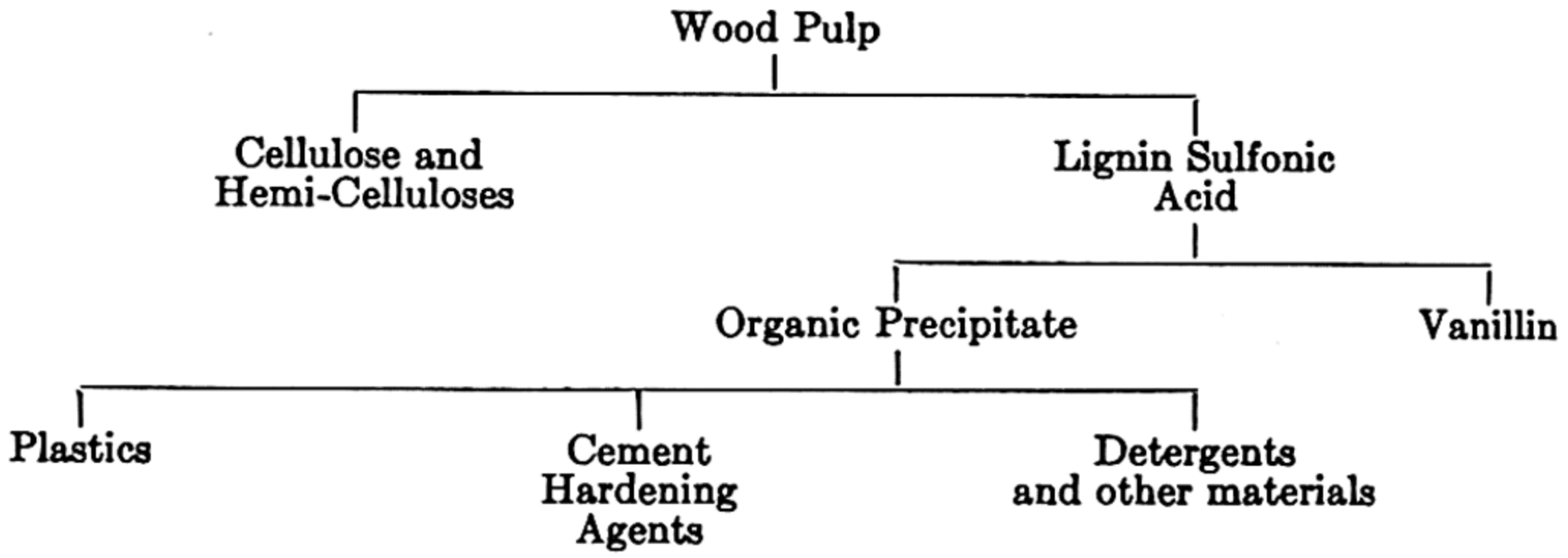
Flavors

Flavors are used for cooking, for candy, chewing gums, beverages, syrups, dental pastes, and medicines. Oil of lemon, of orange, and of lime have been described; they are obtained by expression, and may be freed from the terpenes. Peppermint is made into crême de menthe (Italy). Vanilla extract is perhaps the best-known flavor, and used for numerous purposes. It is made from the vanilla bean, after it has been cured to develop the vanillin content, by extraction with alcohol. The American practice is as follows: 50 pounds of Mexican vanilla beans and 50 pounds of Réunion beans are chipped fine in an automatic cutter, and placed in a "batteuse," a cylindrical extractor of steel, fitted with a stirrer. Thirty-five to fifty per cent alcohol is added, in the cold, and stirred for an hour; the extract is run off, and three further extractions made in the same way. The extracted

[7] Compare *eau de vie*, meaning—whiskey or brandy.

mass is pressed in a wine press and discarded. All four extracts are combined to give the finished material. The amount of 50 per cent alcohol is such that the beans form 10 per cent by weight of the solvent taken. The extract is colored brown by some of the resin which is dissolved.[8]

Vanillin may be made from lignin sulfonic acid, itself obtained from wood pulp; the relationship between several materials obtained from wood pulp is shown on the adjoined chart.[9]



The use of synthetics as flavoring agents is on the increase, as will be seen from the following short list. Methyl anthranilate gives the odor of grapes; ethyl butyrate is basically the odor of rum; safrole, from brown camphor oil, is an artificial sassafras, and is used in root beers, candies, and "herb tonics." Cinnamic aldehyde replaces cinnamon oil, methyl salicylate oil of wintergreen. Frequently used also is benzaldehyde F.F.C. (free from chlorine) as "oil of bitter almond, artificial."

Diacetyl $CH_3 \cdot CO \cdot CO \cdot CH_3$, a yellow, somewhat viscous liquid, and acetyl methyl carbinol, a white, thin liquid, are the chief odoriferous flavor of butter made from sour cream, and are produced by the action of a microorganism. These two substances are now prepared on a large scale, by the action of the same organisms, in special cultures, and are available for flavoring, in cases not prohibited by the pure food laws.

The flavor-accentuating agent, sodium 1-glutamate, is discussed in Chapter 23.

Industrial Perfumery

Odoriferous substances are being used more and more in the general industries and manufacturing, sometimes to render goods more attractive, more often to cover or mask a disagreeable odor inherent in the goods. Examples are: Leather gloves, shoes and handbags, stockings, cotton pads, stationery, wall board (to imitate cedar), lacquer, varnishes and leather dopes, inks, cameras, knit goods, sweaters, and tickings, tobacco, rubber, lubricating oils and greases, kerosine fly and moth sprays, disinfectants

[8] The fresh vanilla bean is green; in size it may be as long as 10 inches; the dried bean is brown. Vanilla beans are shipped tied in bundles of about 30 beans selected of one size. The beans from Réunion, and others, often have a bloom of vanillin on their surface.

[9] A paper on Lignin-Vanillin delivered by J. M. Wenneis, at the 29th annual convention of the Flavoring Extract Manufacturers' Association, June 29, 1938; see also U. S. Patent 2,069,185.

TABLE 114.—*U. S. Production of synthetic flavors and perfume materials (1947).**

	Pounds	Unit Value
Flavors		
Methyl salicylate	2,831,800	$0.34
Vanillin	963,900	3.07
Benzyl acetate	330,600	0.56
Ethyl butyrate	131,300	0.46
Coumarin, synthetic	509,700	2.55
Perfume Materials		
Terpineols	1,074,800	0.33
Ethyl phenyl acetate	579,000	—
Phenyl ethyl alcohol	401,800	1.76
Anethole	363,300	.59
Benzyl benzoate	244,000	.88
Phenyl acetic acid	200,500	1.05
Linalyl acetate	199,400	5.44
Citronellol	161,200	4.13
Piperonal (Heliotropin)	147,100	2.81
Safrol	136,400	.99
Geraniol	102,600	3.62
Methyl ionone	56,700	5.75
α-ionone	11,100	7.99
Ionone, all other	62,900	6.34
Citral	32,900	3.95
Ethyl enanthate	11,600	1.04

* U. S. Tariff Commission.

including para-dichlorobenzene, undertakers' specialties, formaldehyde, shoe and metal polishes, floor-sweeping compounds. Perfumes are often used in ventilating fans, theater sprays and incense. Depending upon the use, the price of the perfume material used will vary from a few cents a pound to $1 a pound.

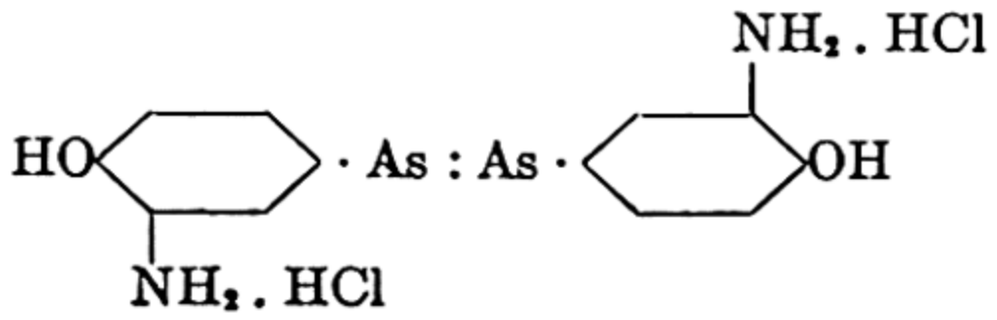
PART II. PHARMACEUTICALS AND ANTIBIOTICS

Closely allied in chemical structure to the flavoring and perfuming agents are the numerous pharmaceutical materials of synthetic and semi-synthetic origin. A number of these, it may be noted, are of very simple chemical structure and inorganic in classification; these are not included. Therapeutic agents produced incident to the growth of living organisms, such as molds, have attained a commanding place among such agents; two of them, penicillin and streptomycin, are discussed in some detail on later pages. They are antibiotic, because they are injurious to the infecting microbes, and hence overcome the bacterial infection itself.

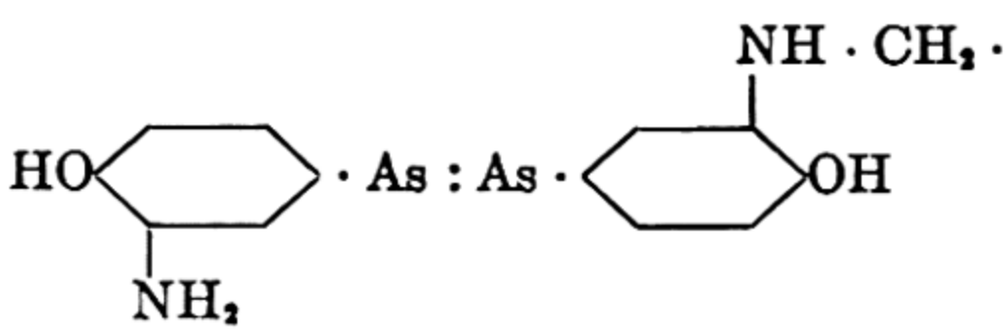
Pharmaceuticals

Any substance used for therapeutic purposes may be classed as a pharmaceutical, so that the list is long. Included in this division are only those which are the products of chemical reactions, in part or in whole, and natural products extracted from plants and animals. Formerly, such pharmaceuticals were chiefly extracted from crude drugs of vegetable origin, and to a lesser degree, of animal origin (cod-liver oil). Today, the natural pharmaceuticals

are supplemented by synthetic products, examples of which are given below; at the same time, new successes in materials of vegetable or animal origin are still comparatively recent, for example insulin, from the pancreas of the steer, for diabetic patients. Arsphenamine (salvarsan), the specific for syphilis, is strictly synthetic; its modern form is neosalvarsan, more stable in air.



salvarsan



neosalvarsan

Quinine sulfate from the bark of the cinchona tree, Peru and Bolivia, is an antipyretic; it is supplemented by the synthetics acetanilide, used for headache powders (Bromo-seltzer), and acetylsalicylic acid (aspirin). Quinine, the antimalarial, scarce during the war, was supplemented by Atabrin (also known as Mepacrine and Quinacrine), then by Chloroquin and by Paludrin. Atabrin is a suppressive drug; generally the skin of the patient turns yellow. Plasmoquin (8-amino quinoline) is a curative drug; it is toxic. Paludrin is a suppressant. Some of the synthetics have to be taken simultaneously with quinine. The narcotic morphine sulfate, the local anesthetic cocaine hydrochloride, the mydriatic (pupil-dilating) atropine sulfate are natural products. Cocaine is now supplemented by synthetic substances, such as procaine hydrochloride (novocaine), and several other similar products, used in dental surgery. Laxatives are still essentially of vegetable origin, for example cascara sagrada bark extract and castor oil; of the synthetic laxatives, phenolphthalein is successfully prescribed. Epsom salt is described in Chapter 12. The important anesthetic liquids, chloroform and ether, which have revolutionized surgery, robbing operations of their terrors, and removing the resistance of the conscious patient, are synthetics of comparatively simple manufacture. As they are both made from ethyl alcohol they might be called semi-synthetic since alcohol is a fermentation product; alcohol may be made from acetylene, when it would be strictly synthetic. The hypnotic paraldehyde is polymerized acetaldehyde, from the distillation of wood; hence it may be called a semi-synthetic. Veronal, a sleeping powder, and saccharin, a sweet non-sugar, are true synthetics. Phenol, formaldehyde, hydrogen peroxide, and iodoform are described in other chapters, radium in Chapter 50.

Ether is made mainly by the dehydration of ethyl alcohol by sulfuric acid; the process is continuous. The sulfuric acid mixed with a certain amount of alcohol is brought to the temperature of 140° C. in a lead-lined steel boiler by means of steam in a closed lead coil; alcohol is vaporized in a separate vessel and the vapor sent through the acid-alcohol mixture in the

still.[11] There passes out a mixture of ether, alcohol, and water, in vapor form, and these are separated in a column still. The water passes out at the bottom. Alcohol, containing some ether and some water (5 per cent), is removed in vapor form half-way up the column, is condensed and used over again in the vaporizer. At the top of the rectifier, ether vapors pass out and are condensed in a separate condenser; such ether contains a small amount of water and alcohol. Sulfur compounds are removed previously, by passing the mixed vapors from the still through a dilute caustic solution. The efficiency of the process is high, about 94 per cent. The reactions are:

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5 \cdot HSO_4 + H_2O$$
ethyl-sulfuric acid

$$C_2H_5OH + C_2H_5 \cdot HSO_4 \rightarrow C_2H_5 \cdot O \cdot C_2H_5 + H_2SO_4$$
ether

The sulfuric acid is regenerated; instead of sulfuric acid, benzene-sulfonic acid has been proposed. A temperature of 128° C. is preferred in a British plant.[12]

Ether is lighter than water and forms an upper layer; it boils at 34.5° C. (94° F.), and chloroform boils at 61° C. Ether is widely used as an anesthetic and as a solvent. Of the medicinal grade, 7.97 million pounds were made in 1935 (U. S.), valued at 18 cents a pound.

Chloroform is more rapid in its anesthetic action than ether; it is more depressing to the heart action. Both are being supplemented more and more with nitrous oxide mixed with oxygen, even in major operations. The anesthesia is begun with ether, for instance, and continued with nitrous oxide, applied at intervals as may be necessary to keep the patient unconscious.

Cocaine hydrochloride is extracted from coca leaves, of the *erythroxylon coca* and related plants, found in Ceylon, Java, Peru, and Bolivia; the content of cocaine base in the leaves varies from 0.7 to 2 per cent. The extraction is chiefly by a mixture of aqueous soda ash and petroleum ether, used warm and constantly agitated in a vessel with stirrer. The alkaloid as the base dissolves in the ether, and is precipitated by hydrochloric acid, as the crude hydrochloride; this is filtered, dried, and sent to the refiners in the consuming countries.

Acetylsalicylic acid, sold in part under the name of aspirin, is made by dissolving salicylic acid [13] in glacial acetic acid, in an earthenware-lined vessel, and adding an excess of acetyl chloride. The vessel or still is jacketed and the contents are heated until the reaction starts, when the steam may be turned off, for the reaction is exothermic. Hydrogen chloride passes out through a worm which condenses the acetyl chloride carried out, and then reaches a small tower where it is absorbed in water. At the end of the action, steam is sent through the jacket and the remaining acetyl

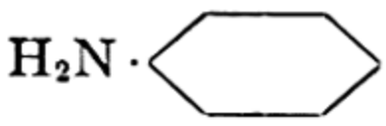
[11] Or an intermediate tower with quartz packing may be used in which the regenerated acid mixes with the alcohol, and the mixture overflows in the still proper; U. S. Patent 1,328,258.

[12] "Organic medicinal chemicals," Barrowcliff and Carr, New York, D. Van Nostrand Co., 1920, p. 128.

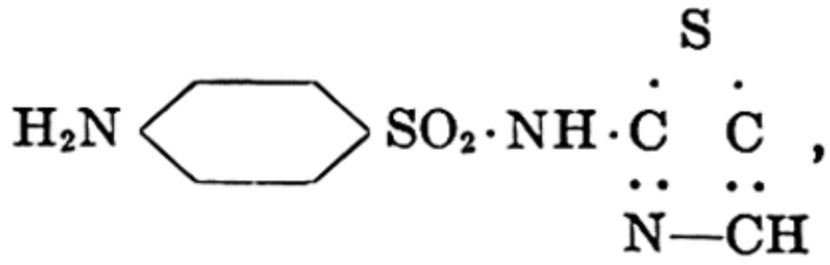
[13] Chapter 27.

chloride distilled. The crude acetylsalicylic acid is left in the still and is purified by solution in alcohol and precipitation by water.

Among the new drugs, sulfanilamide ($C_6H_8N_2O_2S$) or structurally



and sulfathiazole



, both white solids, have rapidly become of commercial importance.

Procaine is made from para-aminobenzoic acid, by forming the diethylaminoethyl ester; the resulting base is insoluble in water, but its hydrochloride is freely soluble. It is used chiefly in the latter form. The successful introduction of procaine hydrochloride as a local anesthetic replacing cocaine and partly sold under the name of novocaine, has led to the preparation of a large number of similar esters, and also of substances with different structures. Methadon is a synthetic pain-killer, rivaling morphine. Like all materials used in pharmacies, a prescribed standard of purity must be reached.[14]

TABLE 115.—*Production of synthetic medicinals in the United States (1947).**
(Items selected for their interest)

	Pounds	Unit Value
Acetylsalicylic acid (aspirin)	12,220,100	$ 0.42
Salicylic acid	6,274,100	.29
Acetophenetidin (phenacetin)	2,283,200	.89
Sodium salicylate	1,233,200	.49
Barbituric acid derivatives, total	900,100	4.63
Ethyl *p*-aminobenzoate (benzocaine, anesthesine)	81,800	3.30
Procaine hydrochloride (novocaine)	42,500	5.81
Neoarsephenamine (neosalvarsan)	19,600	66.26
Medicinal dyes	53,700	14.90
Calcium levulinate	33,700	1.27
Calcium lactophosphate	14,600	—
Iodoform	17,000	4.41
Hexylresorcinol	9,200	—
Bromocamphor	20,000	2.81
Diphenylheptanone (methadon)	900	—
Sulfa drugs, total	6,142,100	4.14
Sulfathiazole	2,697,000	2.97
Grand total, synthetic medicinals, organic	49,624,300	5.52

* U. S. Tariff Commission.

Antibiotics

Antibiotics are antimicrobial agents produced incidentally to the growth of bacteria, yeasts, molds, and other plants. It is in this sense that the term is now in use, although strictly speaking, any agent of whatever origin, which can destroy or inhibit the growth of the living agent of disease, is antibiotic. The most famous antibiotic is *penicillin*, discovered in 1929 by

[14] These standards are listed in the U. S. Pharmacopœia, XIIIth edition (1947), obtainable from the Mack Printing Company, Easton, Pa. The newer remedies are listed separately, in "New and Non-official Remedies," published yearly by the American Medical Association, 535 No. Dearborn Street, Chicago, Ill.

Fleming in England, then left unutilized until 1943, when under the stress of war, its commercial production was undertaken, first in the United States. A second antibiotic which supplements the beneficial action of penicillin and which has been produced since 1946 on large scale, is *streptomycin*. An earlier antibiotic which has been produced commercially for years, and before penicillin, is *tyrothricin*. Several other such products have been introduced and still others are being investigated.

Penicillin is a chemical substance produced in the course of the growth of the mold, *Penicillium chrysogenum*, and has the power to destroy or inhibit any further growth of staphylococcus, streptococcus, pneumococcus and

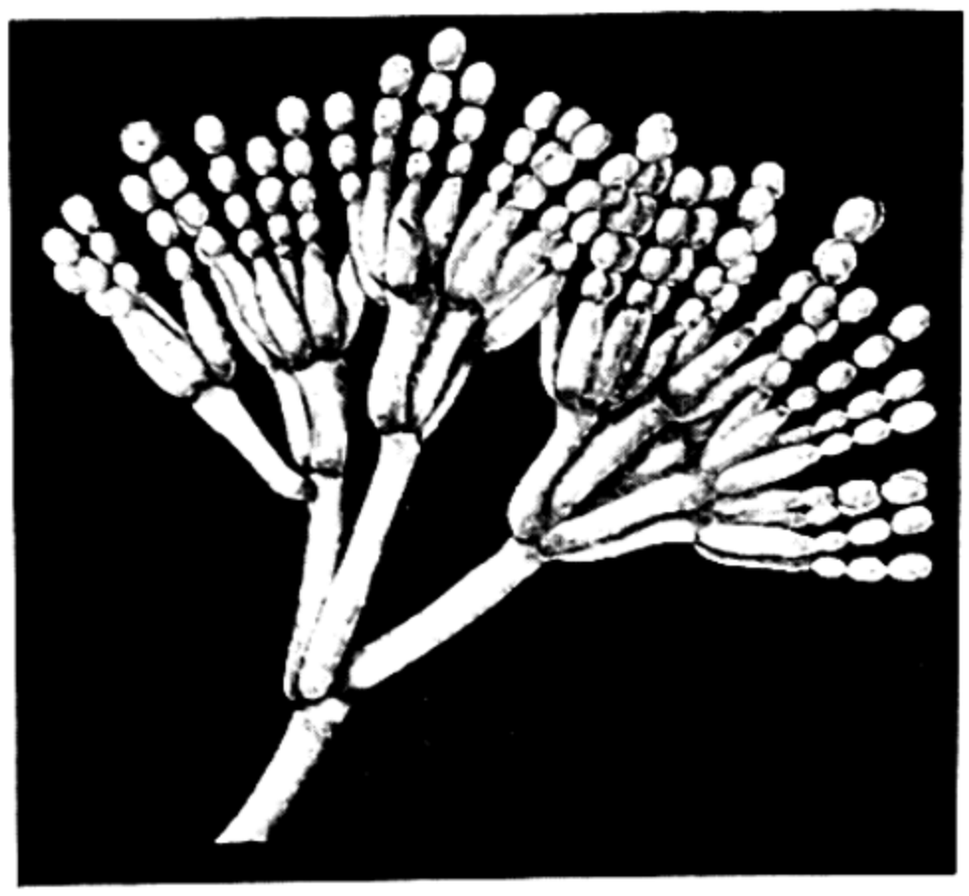


FIGURE 226.—*Penicillium chrysogenum*. Magnification ×150. (Courtesy of Northern Regional Research Laboratory, Peoria, Ill.)

other disease bacteria, which are harmful and often fatal to man. In the treatment of septicemia, until a decade ago the field of promise for the sulfa drugs, penicillin has succeeded where sulfanilamide and other sulfa drugs had failed to cure. Open flesh wounds and wounds in the head, after removal of all débris and treatment with penicillin parenterally and by local application, heal in three weeks, instead of the eight weeks or so previously required. After a serious surgical operation, the patient, if treated by penicillin injection, generally develops no fever. In parenteral application (other than in alimentary organs), the drug is in water solution, as the sodium salt, or in beeswax-peanut oil for slower action. Procaine penicillin, introduced lately, is more slowly absorbed and therefore gives more prolonged action; though relatively insoluble in water, it is prepared as a suspension in suitable fixed oils or as a microcrystalline suspension in water. When taken by mouth, the dose is 5 to 7-fold. Penicillin is also administered in spray form, for infections of the nose and throat. Besides all these successes it may be added that the spirochetes of syphilis are penicillin-sensitive; penicillin is now an important supporting drug to the arsenicals in the treatment of certain types of syphilis, and may supplant these latter agents altogether in the treatment of other types.

The harmful bacteria and other microorganisms which penicillin successfully attacks are mostly gram-positive; against the gram-negative organisms (that is, those which do not respond to the Gram stain) it is generally weak. It is in the treatment of the latter infections that the more

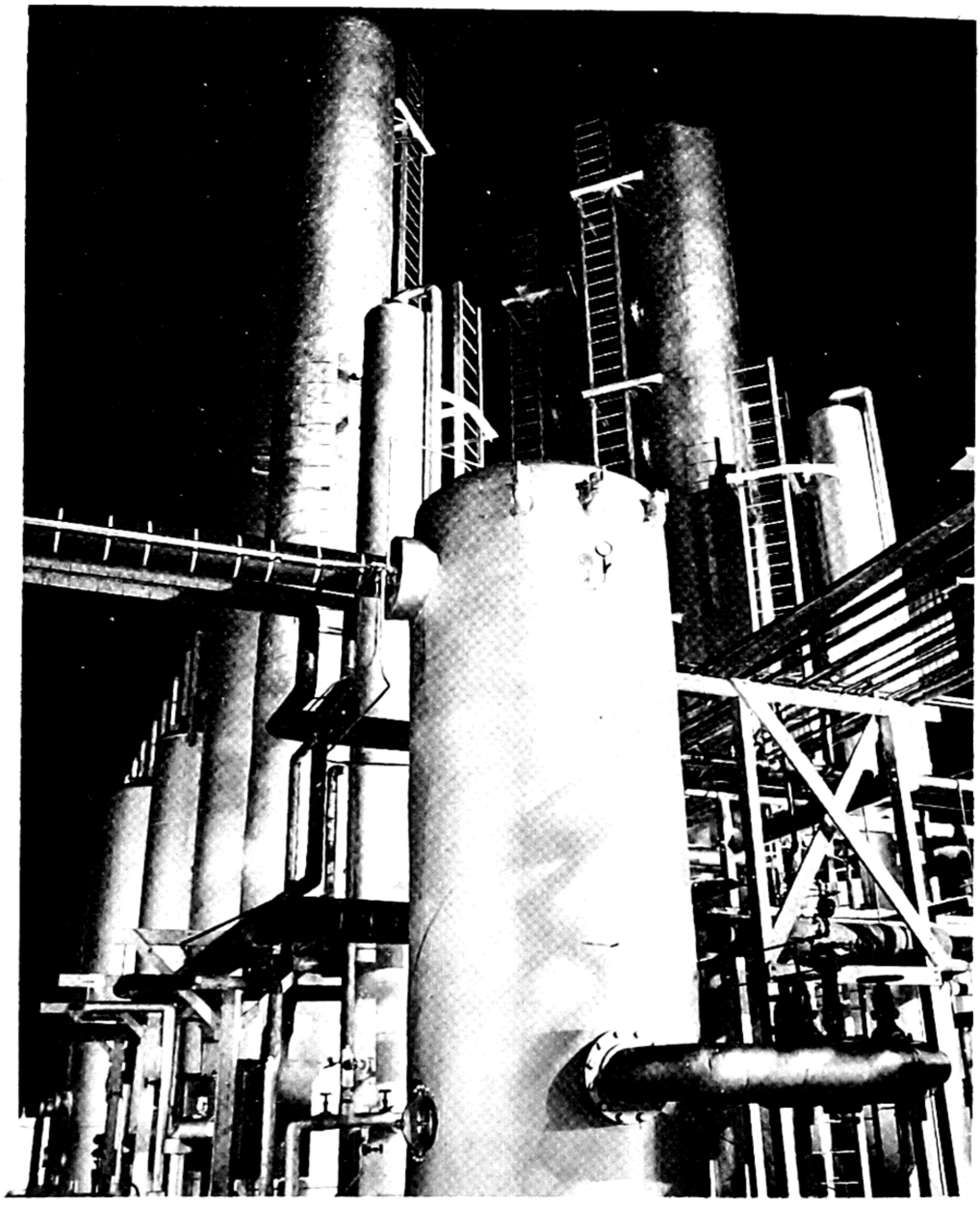


FIGURE 227.—External storage tanks and towers necessary to solvent recovery, air purification and other operations necessary to the mass production of penicillin. (Courtesy Commercial Solvents Corporation, Terre Haute, Ind.)

recently developed antibiotic, streptomycin, in the form of the sulfate, the chloride, or the calcium chloride complex, has found a place. Streptomycin has proved effective against *Hemophylus influenzae*, including urinary tract infections and certain pulmonary ones, while in the treatment of tuberculosis the clinical work has progressed far enough and well enough to say that it is most promising.

Penicillin by Submerged Fermentation: Penicillin is prepared on the plant scale by submerged fermentation, in a battery of steel vessels of 5,000 to

20,000 gallons capacity. The fermentation takes place only in the presence of air, for the mold is aerobic; submerged fermentation is possible only because air is constantly supplied to the fermenters. Each vessel has an agitator, coils for heating and cooling, an inlet for the required air, and a vent for the carbon dioxide formed and excess air.

It is well to distinguish four stages in the manufacture of the drug: (1) fermentation; (2) removal of the mycelium from the fermented broth and

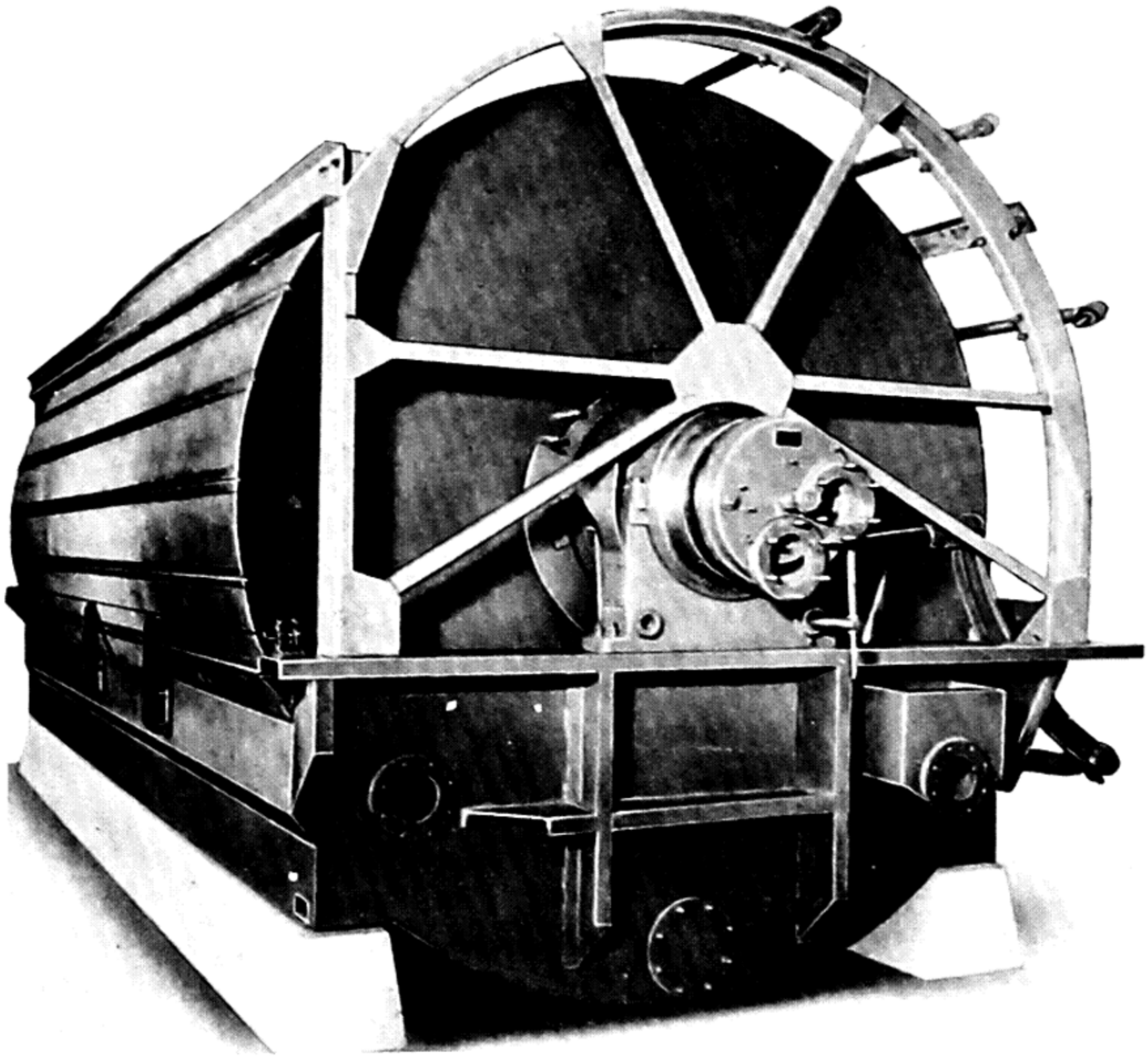


FIGURE 228.—Oliver Continuous Vacuum Drum Filter, panel type, such as might be used to remove the mold mycelium from a penicillin-containing broth.

extraction of the penicillin by solvents; (3) solvent purification and formation of the penicillin sodium salts; (4) testing, storage and shipping. The freeze-drying step which has been described in the literature a number of times, is no longer universal, although it is still practiced by some of the manufacturing companies.

(1) The broth for the fermentation is made from corn steep liquor, by adding 2 to 3 per cent lactose, selected over other carbohydrates because it is *slowly* fermentable, and sometimes other nutrients. After adjusting the pH at 4.5 to 5.0, the broth is charged into the fermenters, where it is sterilized by superheated steam, and then cooled. A culture of *Penicillium chrysogenum* is run in, and sterile air admitted. With the aid of the agitator,

intimate contact between air and broth is secured. A rapid initial production of mycelium is desired. The action is slow; in fact, the complete fermentation cycle lasts about three days. The temperature is held at 75° F. [23.9° C.] by circulating water through the coils. At the end, a 10,000-gallon vessel holds 32 tons of liquid broth, with large quantities of slimy, pale-yellow mycelium, and in solution, ten to fifteen pounds of penicillin.

(2, 3) The content of the fermenter is discharged to a rotary filter, from which the mycelium is removed as a continuous felt, while the clear broth passes to a stainless steel tank for solvent treatment. It was an earlier practice to add at this point activated carbon, which adsorbed the penicillin, and later gave it up to solvents, after a filtration step. In most plants, activated carbon is not used, but the filtered fermentation liquor (the "beer") is treated directly with amyl acetate. For this purpose, the pH is adjusted to 2.5 by the addition of phosphoric acid; the amyl acetate is added and the two liquids emulsified by rapid agitation. The emulsion is separated in centrifuges; of the two layers, the amyl acetate layer which now contains the drug, goes to extractors, meeting a solution of phosphate buffer. The sodium salt of penicillin is formed. Its concentration is higher because the volume of the solvent has been decreased at every step. The purification steps may be repeated. The solution is forced through a Seitz biological filter, whence it reaches a sterilized stainless steel (or glass-lined) container. The crystalline sodium salt of penicillin is produced under sterile conditions, weighed in the form of the dry material and filled into bottles of 20-milliliter capacity; the amount varies with the order, and depending on the amount, the content of each bottle represents from 100,000 to 1 million units of the drug.

(4) Each lot is tested for potency, pyrogens, toxicity and sterility. By a system of numbers, any product which is unsatisfactory can be withdrawn.

At first, the product contained 20 to 30 per cent cf penicillin sodium, and was yellow in color, because there were present, quite harmless, organic substances which had been adsorbed by the activated carbon at that time universally employed. Today the product is practically pure, crystalline, and white, thanks to improvements in technique.

In freeze-drying, a solution of penicillin sodium in an amount (one or two milliliters) computed to give a total of 100,000 units, for example, is charged into 20-milliliter glass containers, under sterile conditions. Within 5 seconds, the bottles are in the freezing machine where the temperature is −70° F. [−56.6° C.]. The ice which formed is removed by sublimation, in high-vacuum cabinets. The purpose of the 20-milliliter capacity bottle is to enable the user to make his solution of whatever strength is required by the addition of pyrogen-free water, without transfer.

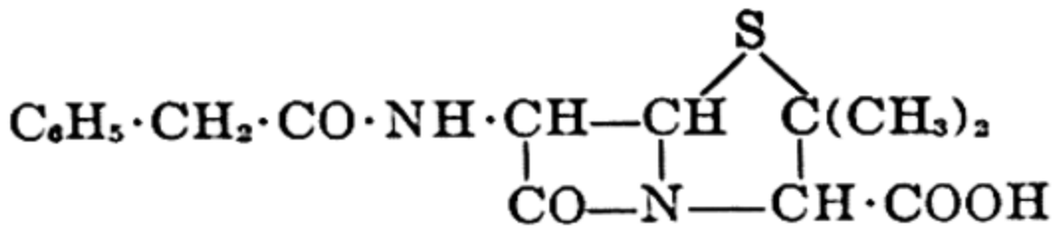
The procedures in several plants differ somewhat from the foregoing; for example, the fermenter may discharge directly into centrifugal baskets, where the separation of the mycelium from the penicillin-bearing broth takes place. In all plants, the solvents are recovered and used over again many times. Besides the sodium salt, the potassium, calcium and procaine salts of penicillin are manufactured.

Penicillin was first produced in 1943; there are now a number of plants in the United States, England, Canada, Mexico, Australia, and other countries. The original U. S. production was 250 billion units a year; for 1946, the production was 25,000 billion units, and the purity, as already mentioned, rose steadily.

The penicillin produced commercially as just described is more precisely designated as *Penicillin G* (benzylpenicillin). There are several different

FIGURE 229.—Test for pyrogens by injecting penicillin solution into ear vein of New Zealand white laboratory rabbit. No significant rise in animal's temperature indicates products' freedom from fever-producing substances. (Courtesy Commercial Solvents Corporation, Terre Haute, Ind.)

penicillins, all produced by the mold. Penicillin G is a strong acid, with the empirical formula of $C_{16}H_{18}O_4N_2S$, and the structural formula below. Penicillin G has been synthesized.



Penicillin G, also called Penicillin II, or Benzylpenicillin

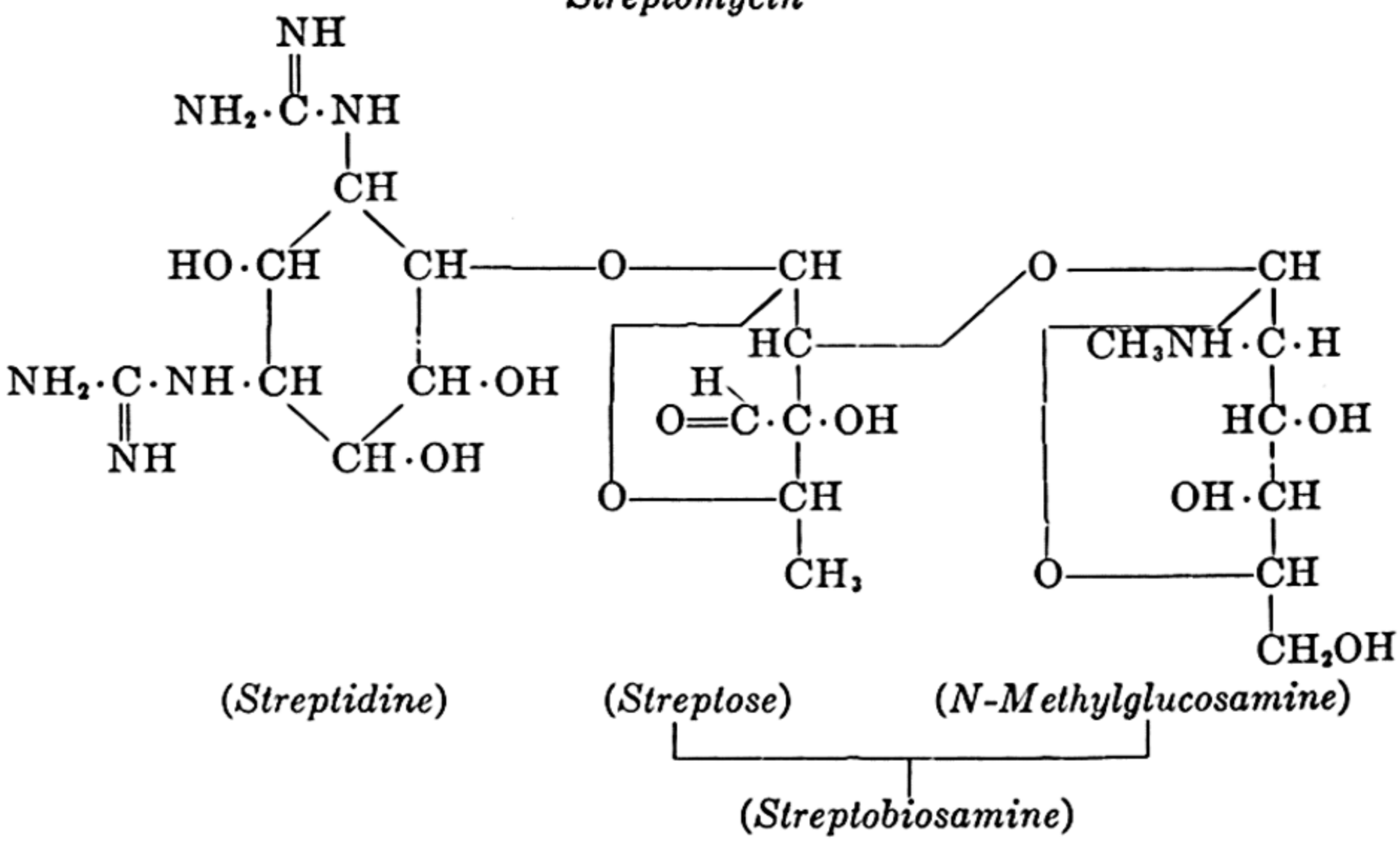
Various units have been employed in evaluating the drug; at the present time, the accepted one is the *International Unit*, defined as that amount of penicillin having the activity of 0.6 microgram of pure sodium penicillin G against a certain strain of *Staphylococcus aureus*.

Streptomycin: Streptomycin, like penicillin, is a chemical substance formed incidental to the growth of a mold, this time, of *Streptomyces griseus*, an aerobic organism. On the commercial scale, it is manufactured by deep fermentation. Streptomycin was discovered by Dr. Selman A. Waksman, of Rutgers University, in 1944, after several years of investigation of soil bacteria. The first commercial plant was erected (by Merck & Co., Inc.) in 1945-1946. There are now five commercial plants (1947), reputed to be in operation, in addition to several pilot plants.

A mash containing glucose, peptone, meat extract or other protein, and salt (NaCl) is sterilized, a culture of *Streptomyces griseus* added, and fermentation allowed to proceed in the presence of large volumes of sterile air, with agitation, at a temperature of 25 to 30° C. (77 to 86° F.). The pH is adjusted to 6.0—6.5 before sterilization. After fermentation, the mycelium is separated from the clear liquid in the presence of a filter aid, in a continuous-pressure type filter. From the clear filtrate, the streptomycin is adsorbed on activated carbon. The streptomycin-bearing carbon is filtered, reslurried with alcohol and again filtered, after which it is made to lose its adsorbed drug to a hydrochloric acid-alcohol solvent, with the formation of streptomycin hydrochloride. Excess acid is neutralized, and the solution concentrated at low temperature. There follow several purification steps. A definite volume of the solution is charged into glass containers; the vials are frozen and then freeze-dried under high vacuum, after which the dry product is tested for potency, sterility, and absence of pyrogens. All these end operations are performed in a sterile area, under aseptic conditions. In addition to the hydrochloride, the sulfate of streptomycin is produced on the commercial scale.

The chemical composition of streptomycin has been established and the formula follows:

Streptomycin



Streptomycin is available in a third form, that of the calcium chloride complex [15] with the hydrochloride; the complex is a white powder, of purity

[15] The calcium chloride complex is manufactured by Merck & Co., Inc., Rahway, N. J.

better than 98 per cent, with the formula $C_{21}H_{39}O_{12}N_7 \cdot 3HCl \cdot \frac{1}{2}CaCl_2$. Its production is reported by weight (in grams and kilograms).

A reduced form of streptomycin (Dihydro-streptomycin) produces fewer neurotoxic effects and allows for more adequate treatment with the drug.

Two recently introduced antibiotics, Chlormycetin and Aureomycin show considerable promise, since they are effective against some Rickettsial diseases, brucellosis, and some gram negative infections which have not previously yielded to either penicillin or streptomycin.

Reading References

"Chemistry and the flavoring industry," Bernard H. Smith, p. 1307; "Relation of chemistry to the citrus products industry," C. P. Wilson, p. 1302; "Chemistry and the cocoa and chocolate industry," Frank C. Gephart, p. 1295; *Ind. Eng. Chem.*, 20 (1928). "Symposium on chemistry and the food industries," in the same volume, pp. 1286-1327.

"Perfumes, cosmetics and soaps," W. A. Poucher, London and New York, D. Van Nostrand Co., Vol. I, 1930, Vol. II, 1932.

"Influence of time of harvest, drying and freezing of spearmint upon the yield and odorous constituents of the oil," Frank Rabak, *Ind. Eng. Chem.*, 10, 275 (1918).

"The essential oils," Horace Finnemore, London, Ernest Benn, Ltd., 1926.

"Observations upon the foreign oil industries of foreign lands," C. A. Browne, *J. Chem. Educ.*, 11, 131 (1934).

"Beiträge zur Synthese des d,l-muscons," L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 17, 1308 (1934).

"The mode of action of sulfanilamide," Perrin H. Long, *Sigma Xi Quarterly*, 29, 150-169 (1941).

"American production of synthetic camphor from turpentine," I. Gubelmann and H. W. Elley, *Ind. Eng. Chem.*, 26, 589 (1934).

"The pharmacological basis of therapeutics," Louis Goodman and Alfred Gilman, New York, The Macmillan Company, 1941.

"Citronellal and hydroxy-citronellal," Dr. K. Bournot, *American Perfumer*, March, 1937.

"Penicillin and other antibiotics," Wallace E. Herrell, Philadelphia, W. B. Saunders Co., 1946.

"Penicillin," T. H. M. Taylor, *Chem. Eng. Progr.*, 43, 155 (1947).

"Penicillin production by submerged fermentation," Staff report, *Ind. Chem.*, 22, 329 (1946).

"Freeze-drying (Drying by Sublimation)," by Earl W. Flosdorf, Reinhold Pub. Corp., New York, 1949.

"Modern cosmetics," Francis Chilson, *Drug and Cosmetic Industry* (1938).

"The science and art of perfumery," Edward Sagarin, New York, McGraw-Hill Book Co., 1945.

"Natural Perfume Materials," by Y. R. Naves, trans. from the French by Edward Sagarin, Reinhold Pub. Corp., 1947.

"The Chemistry of Penicillin," report on a collaborative investigation by American and British chemists, Hans T. Clarke, John R. Johnson and Sir Robert Robinson, editorial board, Princeton, Princeton University Press, 1949.

That the preparation of protective coatings for steel and lumber is an important industrial activity is apparent when it is considered that the interior and exterior of buildings, railway and motor cars, the bottoms as well as the superstructure of ships, and the cables, girders, and arches of bridges are so treated. The chemist-technologist has been active in this field and made important contributions in the form of improvements and discoveries.

Chapter 31*

Pigments, Paints, Varnishes, Lacquers, Printing Inks

Pigments

The pigment industry is usually thought of as associated with paints, but it is really a separate industry which should be considered by itself, for although a considerable tonnage of pigments is mined or manufactured for use in paints and enamels, almost as much is consumed in rubber goods, linoleums, oil-cloth and artificial leather, plastics, ceramics, and other articles.

Among the white pigments, titanium dioxide stands in first place; its production surpasses that of zinc oxide, which in turn exceeds that of white lead, the leader of yesteryear; the tonnage of lithopone equals or even surpasses (in 1946, for example) that of zinc oxide. The production of litharge is four times that of red lead. Carbon black is the leading black pigment. The oxides of iron, both natural and synthetic, are produced in large quantities. Prussian Blue and Phthalocyanine Blue are the prominent blues, with ultramarine used in smaller amounts. Lead chromate (yellow), chrome oxide (green) and other chrome greens are used for color to a great extent; several of the older natural pigments continue to give service. Metallic salts of organic dyes, among them other phthalocyanines, are being used to an increasing extent. For ceramics, metallic oxides are in demand. The role of pigments in paints, enamels, lacquers and printing inks is presented in this chapter; other uses of pigments are discussed in appropriate places.

White Lead

White lead is a basic carbonate of lead, that is, a carbonate combined with the hydroxide. Its formula is $2PbCO_3 \cdot Pb(OH)_2$, but the variations from this are considerable. It is better to remember it merely as a basic carbonate.

White lead is prepared by several methods and many of those developed at the outset of the industry are still in vogue.

The Dutch Process. Lead, in the form of cast buckles, is corroded by the vapors of acetic acid and water in the presence of carbon dioxide emanating from fermenting tan-bark. Lead acetate, the first compound formed, is transformed by the carbon dioxide and moisture partly into lead carbonate and partly into lead hydroxide.

* In collaboration with Mr. William G. Ringle, Enamel Research Department, Pratt and Lambert, Inc., Buffalo 7, N. Y.

The buckles are placed in small earthenware crocks 8 inches in diameter and 10 inches high, into which a pint of 28 per cent acetic acid has been poured. The buckles lie over the acid, resting on a small shoulder in the inner wall of the crock. A layer of these crocks is placed in a thick bed of spent tan-bark, then covered by boards, over which more tan-bark is shoveled, followed by another tier of crocks. This is repeated until 10 or more tiers are made ready. Some ventilation to the center is provided by a stack-like opening in the middle. The room is then closed. Fermentation of the tan-bark proceeds and the temperature rises perhaps to 70° C. The pots remain undisturbed for three months. After that time they are unpacked, and the buckles, now white, lifted out, crushed free from any uncorroded center, and ground dry or wet.

The Dutch Process is slow and requires much hand labor. Extremely pure lead is required; otherwise the corrosion does not proceed far enough. However, the high quality of the product obtained by this process justifies its continuance.

The Carter Process. Melted lead is atomized by superheated steam very much as oil is atomized in an oil burner; it is then placed in wooden cylinders lying on their sides and rotated slowly. At intervals dilute acetic acid and carbon dioxide from a coke fire are fed in with some air. After 6 to 7 days, the lead is corroded and has become white lead. This process, which eliminates the need for tan-bark, avoids possible contamination.

The French Process. Litharge (PbO) is dissolved as a basic lead acetate in acetic acid and carbon dioxide (fire gases) is pumped into the solution. The basic carbonate (white lead) precipitates and is filtered off. The lead salts remaining in solution are not lost, as the filtrate is used in the next batch.

For comparison, the Dutch Process requires 3 to 4 months; the Carter Process, 1 week; the French Process, 1 or 2 days.

In the Rowley process, no acetic acid is used; atomized lead suspended in water is exposed to warm air, when the hydroxide forms. Carbon dioxide is pumped in and white lead of good covering power is produced. The Sperry process is an electrolytic process.

A serious shortage of lead during World War II made the following process of interest: [1] A mixture of extremely fine silica and tribasic lead sulfate or lead oxide is furnaced for two hours at 625° C. There results a silica which is surface-coated with monobasic lead silicate and monobasic lead sulfate. By this means, three times as much pigment can be made from the same amount of lead.

White lead is usually wet-ground, as the dry dust constitutes a health hazard because of its poisonous nature. After wet-grinding, the suspended solid is thickened by settling, giving "pulp lead." If it is intended for paint purposes, linseed oil can be mixed with the pulp. The oil displaces the water and the resulting paste is ground on roller mills and sold as lead-in-oil. The pulp may also be dried and disintegrated and sold as a dry powder.

[1] Presented at 1947 A.C.S. meeting and abstracted in *American Paint Journal* (by J. J. Williams and A. R. Pitrot, Nat. Lead Co.) 31, No. 52, 76 (1947).

Zinc Oxide

Zinc oxide is made in several ways. The original one, still in use, is the French or indirect process, in which zinc metal (spelter) is heated in stoneware retorts, the metal vaporized and burned in a combustion chamber placed at the mouth of the retort. An exhauster draws the white dust to an air chamber first, where the heavier, less desirable particles are deposited, then to a filter chamber, where the fine dust is collected.

In order to obtain the whitest pigment, a very pure spelter must be used; if it contains lead, for instance, a frequent impurity in zinc, the lead burns to litharge and gives a yellowish tinge, a serious fault. To render the lead harmless, a modified indirect method has been developed, in which the burning is done in air mixed with carbon dioxide; the lead is changed to

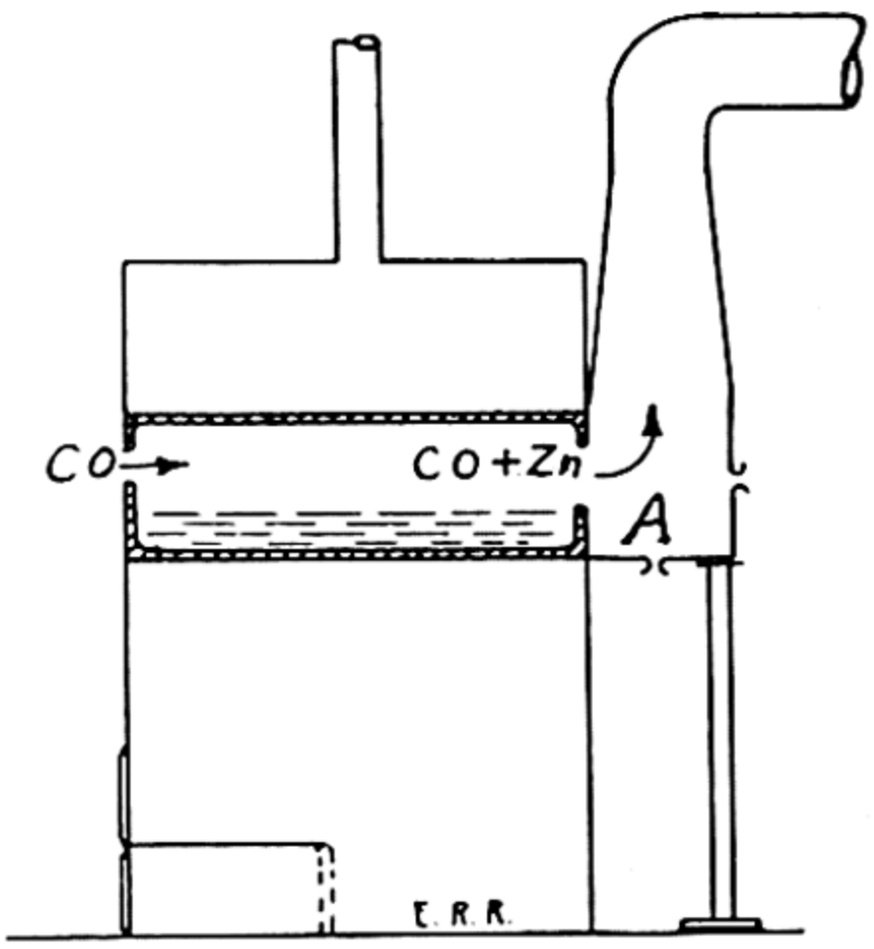


FIGURE 230.—Retort for vaporizing zinc in a stream of carbon monoxide; the two are burned together in the combustion chamber *A*, to manufacture zinc oxide.

white lead and thus the yellow tinge is avoided. The zinc oxide is unaffected. This modification has been extremely successful and has made possible the use of spelters containing appreciable quantities of lead.

Another modification is to use a retort open at both ends, and to send in at one end carbon monoxide, which passes over the heated metal and assists in its vaporization. The two burn together as they issue from the other end of the retort into a combustion chamber; the resulting flame is an intense yellow-white. A simple sketch (Fig. 230) shows the disposition of the apparatus. An exhauster pulls the fumes through a cooling chamber and forces them through bag filters.

A direct process, that is, one producing the oxide directly from the ore, was developed by Mr. Weatherill about 80 years ago for the New Jersey Zinc Company. In the Weatherill furnace, designed for this purpose, franklinite, an oxide of zinc containing also iron and manganese (Zn 18 per cent), mixed with coal is burned on a grate; the natural oxide is first reduced and then re-formed by the air and carbon dioxide from the fire. Provision is made to admit more air over the fire if unburned zinc vapors should rise. The grate is a casting with tapering holes, not bars. The residue on the hearth is made into spiegeleisen, a manganese-iron mixture which also contains carbon.

It is feasible to use a low-grade carbonate ore (smithsonite) for the direct production of zinc oxide. In such a plant at Leadville, Colorado, 2000 pounds of ore are well mixed with 1100 pounds of coal and wetted to have 20 per cent moisture; this batch is shoveled onto the grate of a Weatherill furnace on which a coal fire is burning. Air is forced into the closed ash-pit; the temperature is 1000° C.; the burning requires 6 hours. The gases which pass out with the dust are cooled in a U-shaped 4-foot-diameter flue, 600 feet long. At the end of the trip, the gases are at 140° C.; an exhauster sends them into cotton filter bags 20 feet high by 2 feet wide, which retain the dust, while the gases and water vapor pass out.[2]

Lithopone. Lithopone is formed when a solution of zinc sulfate is mixed with one of barium sulfide; barium sulfate and zinc sulfide are formed; they are both white: $ZnSO_4 + BaS \rightarrow BaSO_4 + ZnS$. This precipitate is not suitable for a pigment, however, until it has been dried, heated to a high temperature in a muffle furnace, and plunged when still hot into cold water. Lithopone is 30 per cent zinc sulfide and 70 per cent barium sulfate, with slight variations; it has fair covering power, is brilliant white, and is cheap. It is used extensively in interior wall coatings.

Titanium Dioxide

The use of titanium dioxide, a brilliant white pigment, has increased year by year; since 1939, it has been utilized in greater quantity than any other white pigment.

Titanium ores are very widespread. The chief ones are ilmenite ($FeTiO_3$) and rutile (TiO_2). Ilmenite is obtained from sand in Florida (near Jacksonville); from deposits in Virginia (Nelsonite); and in North Carolina. A deposit in New York (Tawahus) is still being worked. Considerable amounts of the ores are imported. Compared with a domestic production of concentrates of ilmenite of 282,447 tons in 1946 (with 46 per cent TiO_2), the imports of ilmenite were 242,340 tons. The corresponding figures for rutile are: 7,453 tons against 5,864 tons. Imports from India in 1947 were 262,000 tons of ilmenite ore and the figure was slightly higher in 1948 (estimated). A large ore body containing iron oxide and titanium oxide has been discovered in Eastern Quebec,[3] which will probably be a large factor in 1950 or 1951.

The pigment is usually prepared from the concentrated ore by mixing with sulfuric acid; the reaction which takes place is exothermic and violent. The soluble sulfates are treated to reduce the iron to the ferrous state; and much of the ferrous sulfate is removed by crystallization. The clarified liquor is concentrated in vacuum evaporators, then boiled with sulfuric acid when the titanium dioxide precipitates. The pigment is washed, dried and calcined at a temperature of about 900° C. The calcining operation converts

[2] *Met. Chem. Eng.*, 13, 631 (1915).

[3] The deposit is estimated at 125,000,000 tons of high-grade ilmenite (35% TiO_2), and is situated in the Allard Lake region, about 25 miles from Havre St. Pierre on the St. Lawrence river. From here it is shipped by boat to Sorel. The refining process proposed is a reduction of the iron to the metal in electric furnaces, with a production of a slag which will contain the titanium oxide, to be treated further for the production of the white pigment.

the titanium dioxide from the amorphous to the crystalline state, and at the same time raises the refractive index. The higher index raises the hiding power of the pigment.

A more recent advance in titanium pigment manufacture is the production of the rutile crystal structure by chemical methods. The rutile structure has a refractive index of 2.72, while the anatase structure has an index of 2.55; the former has a tinting strength and hiding power about 25 per cent greater than the latter (see Table 116) in oleoresinous vehicles.

TABLE 116.—*Relative tinting strength of the more common white pigments.*
(H. A. Gardner)*

Titanium dioxide, rutile crystal form	1600
Titanium dioxide, anatase crystal form	1275
Zinc sulfide	850
Titanium calcium, 30% TiO_2, rutile form	600
Titanium calcium, 30% TiO_2, anatase form	460
Lithopone, regular	280
Zinc oxide	170
White lead, regular	140

* "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," Eighth ed., p. 92, Inst. of Paint and Varnish Research, Washington, 1937.

Titanium dioxide, both rutile and anatase, is frequently extended with an "inert" or non-hiding pigment. Calcium sulfate is the most common extender used. The composite pigment contains 30 per cent TiO_2 and 70 per cent $CaSO_4$. It is prepared by two methods (1) by precipitating hydrated TiO_2 in the presence of $CaSO_4$, the co-precipitate being filtered and washed, followed by calcining and dry grinding. (2) TiO_2 and $CaSO_4$ may be mixed as a wet slurry, filtered, dried, calcined, and dry-ground.

Titanium dioxide in the pure state or as a composite pigment is widely used in the paint, paper, rubber, ceramic, floor covering, and cosmetic industry. Its chief value stems from its bright, white color and opacity or hiding power. The tinting strength and opacity of titanium dioxide surpass that of any other white pigment.

It is now possible to control "chalking" or rate of weather erosion of TiO_2 pigments. This controlled-chalking feature makes it practical to incorporate TiO_2 in exterior paints and take advantage of its color and hiding properties. A controlled-chalking pigment may be prepared by calcining TiO_2 in the presence of antimony oxide (Sb_2O_3) or alumina (Al_2O_3).

Titanium dioxide paints having controlled chalking are currently very popular for house paints, as they stay white longer because of the gradual erosion of the soiled surface. Titanium dioxide is usually combined with white lead and other pigments for this purpose.

All the pigments discussed so far in this chapter are white: white lead, sublimed white lead, zinc oxide, leaded zinc oxide, titanium dioxide, lithopone. These pigments are similar not only in their white color, but in their quality of opaqueness and hiding power in oleoresinous vehicles; they are the basis of most of our exterior house paints, and of many of our interior paints and enamels. Blanc fixe ($BaSO_4$) is also white in color, but has no hiding power

in oleoresinous vehicles; it is used as an extender. Other extenders are magnesium silicate, whiting (finely divided calcium carbonate), finely divided silica, etc. It should be noted that such inerts in oleoresinous vehicles (blanc fixe, calcium sulfate, calcium carbonate, aluminum silicate, magnesium silicate, silica, and others) do have hiding power where their refractive index differs from that of the vehicle in which they are dispersed, *e.g.*, calcimine paints and whitewash. A few examples of the more common colored pigments follow.

Colored Pigments

Litharge. Litharge (lead oxide) may be prepared in several ways. The oldest method, still practiced, is to heat lead metal in a low-arched reverberatory furnace with the usual bridge wall dividing the fireplace from the hearth. The atmosphere is kept oxidizing by allowing much air to enter; the temperature is just above the melting point of lead oxide (PbO). As the oxide forms, it floats on the surface and is pushed to one side by iron hoes. When enough oxide has collected, it is drawn off by means of the hoes, cooled, ground, and levigated. The color is buff. A continuous furnace has been successful, in which air jets impinge on the surface of the lead so as to sweep the molten oxide to the front end of the oval furnace; fresh lead is added in a stream so regulated that the amount of lead in the furnace remains constant. The molten oxide overflows into a conical receiver; its content when cold is broken up, ground, and air-floated to remove unoxidized lead particles.

Litharge is also made as a by-product in the manufacture of sodium nitrite. Sodium nitrate is melted in a large iron pot, kept at 340° C. Lead in thin plates is added. After they have disappeared, the heat is maintained 20 minutes; the brown mass formed is then cooled and extracted with water, and sodium nitrite crystallized from the decanted solution. The residue is litharge; it is washed, and used for red lead or as is.

Red Lead. Red lead is made by calcining litharge in a muffle furnace into the muffle of which a current of air is admitted. The temperature must be maintained within narrow limits, near 340° C. The period is usually 48 hours.[4]

Carbon Black. There are several kinds of carbon black: *thermal black*, produced by the thermal decomposition of natural gas; *channel black*, by the impingement of numerous small, regulated flames against a relatively cold steel surface, constantly scraped free of the deposit; *furnace black*, by the partial combustion of the gas in a furnace, recovery of the carbon product in cyclones and electrical precipitators.[5] Other blacks are *lampblack*, used mainly as a tinctorial pigment, and *oil black*. Thermal black is used as a filler and an extender in rubber. Until recently, channel black has been the important rubber compounding black. After the introduction of the synthetic GR-S, and more recently of "cold rubber," it has been found that certain furnace blacks with particle size larger than that of the standard

[4] "The lead and zinc pigments," C. D. Holley, New York, John Wiley and Sons, Inc., 1919.

[5] Flowsheets will be found in *Chem. Industries*, 64, 42 (1949).

channel black (such as 100 to 45 millimicrons), gave superior reinforcement. The great advantage of furnace black is that its yield is higher (as high as 8 pounds per 1000 cu ft of gas) than that of channel black (1 to 2 pounds fer 1000 cu ft of gas).

TABLE 117.—*Production of carbon black from natural gas (U. S.).*
(Minerals Yearbook, 1946)

	1942 pounds	1946 pounds
By contact processes, principally channel	428,665,000	619,109,000
By furnace processes principally furnace black	145,341,000	625,312,000*
Average yield of carbon black produced/1000 cu ft	1.71 lb	2.44 lb
Average value of carbon black produced	3.41c	4.82c
Average value of natural gas per 1000 cu ft	1.29c	3.02c

* Of the total 1,244,421,000 lbs, 830,850,000 lbs were produced in Texas, and of that figure, 596,678,000 lbs in the Panhandle; also, 191,857,000 lbs were produced in Louisiana.

Carbon black may be pelleted by a dry or a wet process, for greater convenience and success in handling. Thus, carbon blacks which have been treated with zinc naphthenates, and the "beaded" blacks, from which entrapped air has been removed, can be wetted much more quickly and effectively by the vehicle.

Lampblack is an older pigment; it has been made for thousands of years by the Chinese, Egyptians and other ancient races for the manufacture of ink. It consists of the free soot or smoke collected in chambers from burning oils or hydrocarbon gases. In many of its earlier uses, it has been displaced by carbon black.

TABLE 118.—*Distribution of carbon black, by industries.**
(Domestic deliveries)

	1942 lbs	1946 lbs
To rubber companies	295,947,000	941,464,000
To ink companies	19,233,000	29,561,000
To paint companies	3,616,000	9,312,000
For miscellaneous purposes	15,500,000	18,318,000
Export	115,635,000	271,085,000
Total sold	449,931,000	1,269,740,000

* Minerals Yearbook, 1946.

Iron Oxide. Iron oxide (Fe_2O_3) is made on a large scale by roasting ferrous sulfate obtained from the pickling vats for steel. Water and sulfur oxides are driven off and led through a stack to the atmosphere. The shade can be varied by altering the firing time, the temperature and the atmosphere. It is a relatively cheap pigment and is usually used in red barn paint and metal prime. The use of selected grades for polishing glass and lenses is based on their freedom from grit and the hardness of the glass: such grades of iron oxide are called rouges.

Prussian Blue. Prussian blue or iron blue is manufactured by reacting sodium ferrocyanide, ferrous sulfate and ammonium sulfate. The precipitate is then oxidized with sodium chlorate or sodium dichromate.

Phthalocyanine Blue. Copper phthalocyanine blue is considerably more expensive than Prussian or ultramarine blue, but because of its high tinting strength and color permanence, its use is expanding.[6]

Chrome Yellows. Chrome yellows are prepared by precipitating a soluble lead salt from solution by the addition of sodium or potassium dichromate. They are clean, bright colors having a high tinting strength. The shade may be varied by adjusting the pH of the precipitating solution.

Chrome Greens. Chrome greens are manufactured by coprecipitating Prussian Blue and Chrome Yellow. Their color is dependent upon the proportions of the two pigments used.

Among the natural pigments still in use are umber (brown), ochre (a poor yellow), and Sienna (a deeper yellow).

TABLE 119.—*Production (sales) of lead and zinc pigments (U. S.).**

	1946	
White lead, dry and in oil	66,501 tons†	$207
Litharge	133,799	175
Red lead	32,526	196
Zinc oxide	157,851	144
Leaded zinc oxide	67,971	143
Lithopone	147,001	81

* Minerals Yearbook.
† Includes basic white lead.

TABLE 120.—*Titanium ore requirements for titanium pigments (1946).**

	Short tons Ilmenite	Estimated TiO_2 content
Manufactured titanium dioxide pigments used	390,042	200,352 tons
No production reported from rutile		

* Minerals Yearbook.

PAINTS

A paint consists essentially of a pigment suspended in a vehicle. Its purpose may be protective or decorative, or both. Modern paints are "tailor-made" coatings which are usually designed by skilled scientists for specific purposes. Exterior paints generally lack the esthetic qualities demanded by decorators and architects for the interior of homes and institutions. On the other hand, interior paints as a class would not be sufficiently resistant to the corrosive action of rain, frost, sunlight, or industrial fumes —a resistance which is expected of an exterior paint.

The usual components of ready-mixed exterior house paint are pigments, "semi-drying" and "drying" vegetable oils, driers, and a solvent. Certain paints also contain resins. It is one of the functions of the oil to give the paint elasticity, so that the coating may withstand the expansion and contraction induced by temperature changes without cracking and chipping.

Paints "dry" by oxidation and polymerization of the vehicle, which is hastened by the incorporation of driers. These are catalysts which consist usually of the naphthenates, oxides, resinates, or oleates of cobalt, lead, manganese, iron, calcium or zinc.

[6] *Ind. Eng. Chem.*, 31, 839 (1939); see also Chapter 28.

Solvents such as, for example, mineral spirits, or turpentine are added in various amounts to decrease the viscosity of the paint, making it possible to apply it in thin, uniform layers, or to spray it onto a surface, or to use it as a dip. As to the pigment, its function is to give the paint opacity, color and added durability, the latter in part at least by protecting the oil and resin film from ultraviolet light, and, with respect to zinc oxide, by the protection afforded by its fungicidal properties.

Pigments frequently used for their protective and opaque characteristics are white lead, zinc oxide, titanium dioxide, lithopone, red lead, and iron oxide. To these pigments, small amounts of tinting colors are often added for decorative purposes. The relation between the refractive index and hiding power has been illustrated earlier in the chapter. Invariably, a white paint formula will list at least three different white pigments; included will be an inert, as for example, magnesium silicate, which has several valuable functions. One of these is to prevent too rapid settling of the other pigments; another is to aid in protecting the paint from weathering.

Examples of mixed white pigments for exterior house paint: (1) 15 per cent titanium dioxide; 30 per cent white lead; 30 per cent zinc oxide; 25 per cent inerts (siliceous). (2) 15 per cent titanium dioxide; 47 per cent zinc oxide; 38 per cent inerts. (3) 15 per cent titanium dioxide; 40 per cent lead free zinc oxide; 45 per cent inerts (siliceous).[7]

TABLE 121.—*A formula for an exterior house paint.**

Paint, exterior, house	Total formula	Pigment 61%	Vehicle 39%
Basic sulfate-white lead	11.1%	18.2%	—
Zinc oxide	20.7	34.0	—
Titanium dioxide	10.5	17.2	—
Magnesium silicate	13.5	22.2	—
Silica	5.1	8.4	—
Linseed oil	29.7	—	76
Driers	.7	—	1.8
Mineral spirits	8.7	—	22.2
	100%	100%	100%

* From Pratt and Lambert, Inc., label, March 1949, subject to change at any time.

There are several methods for the preparation of paints, all of which strive for a homogeneous dispersion of the pigment in the vehicle.

One of the most efficient factory layouts consists of utilizing a four-story building, which permits gravitational flow of the raw materials and finished products through the plant. The pigments and grinding liquids are stored on the top floor, whence they can be fed by means of chutes to the mills, which are located on the floor below. After the grinding or dispersing action is completed, the paint is discharged from the mills through chutes or pipe lines to storage tanks on the floor below. The "floor tanks" have agitators to keep the mix from settling; for certain formulas, additional vehicle is

[7] "Post-war exterior house paints," S. Wertham, *Paint and Varnish Prod. Manager, 27,* 115 (1947).

added in these tanks. Here the batch is held until quality control tests are completed; it is then strained and filled into shipping containers, and sent to the ground floor, which is used for shipping and warehousing.

The three most common methods for paint preparation are as follows:

(1) *Roller mill grinding.* In the United States three-roll and five-roll mills are widely used; they consist of a series of water-cooled, hardened steel rollers. The rollers turn at different speeds and each roll turns in the opposite direction to the rolls adjacent to it. There is a very small clearance between the rolls. A scraper blade on the last roll removes the well mixed paste, to which additional vehicle is incorporated.

(2) *Pebble mill grinding.* The pigment and vehicle are placed in a porcelain-lined, water-cooled pebble mill (Chapter 44). The mill is about half full of pebbles, which are about the size of golf balls. The mill is then rotated until the desired fineness of dispersion is obtained; the time may vary from 4 to 48 hours, 16 to 20 hours being the most common. The pebbles impinge against the walls of the mill and against each other, thus reducing the size of the agglomerates in the pigment and vehicle mix. The capacity of the pebble mills for this purpose may vary from 5 to 500 gallons, with 300 gallons the general one.

When blacks or colored paints are ground, the grinding time can be shortened by replacing the pebbles with steel balls. The pebble or ball mill is the most economical grinding method. Occasionally a buhrstone or steel lining is used in the mill in place of porcelain. The steel lining increases the speed of production but discolors the whites to some extent.

(3) *Stone mill grinding.* This method is still used but in a restricted degree; its slowness increases the cost of production. A more modern yet similar method is the Hy-R-Speed mill, using silicon carbide stones about 10 inches in diameter. One of the stones turns rapidly while the other remains stationary. The paint is drawn between the stones by means of rotating fins.

Emulsion Paints. Emulsion paints are of two main types: either the paint vehicle with its pigments is emulsified in water, or water may be emulsified in the paint. There are advantages to such emulsions; one is that the paint may be thinned with the universally available liquid, water. A third type of interest, especially during the war, is the emulsifiable paint.[8] The protein products casein and (more recently) soya protein, are often used as a base for such emulsion paints.

Varnishes and Enamels

Varnishes. By the term "varnishes" is meant here the clear, oleoresinous coatings made by cooking drying oils and resins, and then adding driers and thinners. The most characteristic drying oil used for these varnishes is tung oil, while the resin is ester gum, "Pentalyn," or a special synthetic resin. A paint, on the other hand, as represented by the ordinary exterior house paint, has linseed oil as vehicle, and contains no resin. The oleoresinous varnish manufacturer is not limited to tung oil; indeed over the period of the war, he was forced to use dehydrated castor oil, synthetic drying oils, and

[8] "Emulsion paints," George M. Sutheim, *Chem. Industries*, 60, 948 (1947).

linseed oil as far as obtainable. As indicated in Table 111 tung oil is rapidly regaining its position. Tung oil, heated for 5 minutes at 550° F. (288° C.), cools to a solid gel, whereas linseed oil, heated for several hours at the same temperature cools to a viscous liquid.

A relatively new oil is oiticica oil, from Brazil, which dries faster to a harder film than linseed, but not as fast nor so hard as tung. (Drying oils, as well as semi-drying oils, synthetic drying oils and non-drying oils, have been presented in Chapter 29). Soybean oil in its capacity as semi-drying oil, dries too slowly for general use in varnishes, but when made into an enamel, it yellows less upon aging than many other oils. It is used, however, in baking enamels, and as the fatty acid in alkyd resins. The composition of the fatty acids in soybean oil follows:

Palmitic acid	6.5%	saturated
Stearic acid	4.5	saturated
Arachidic acid	0.7	saturated
Oleic acid	33.5	unsaturated
Linoleic acid	52.5	unsaturated
Linolenic acid	2.3	unsaturated

The first four acids are desirable for edible purposes, while the two remaining ones are paint oils. It is the low linolenic content in soybean oil which is responsible for the non-yellowing of paints which contain it.

The principal varnish resins, in addition to those mentioned, are Congo copal, a natural resin, rosin and rosinates. The Congo copal is a fossil resin, and is dug out of swampy ground in the Belgian Congo. Similar resins of lesser importance are Manilla copal from East India, and Kauri from New Zealand. The synthetic resins which are suitable are all oil-soluble, and include modified and unmodified phenolics, maleic, alkyd coumarone, petroleum, and terpene resins. The oil imparts elasticity, toughness and weather resistance, while the resin contributes hardness and gloss.

The modified phenolics of special interest here are phenolformaldehyde resins, in which the "phenol" is para-tertiary butyl phenol, para-tertiary amyl phenol, para-phenyl phenol, or bis-phenol.

Rosin (Chapter 16) is widely used in the varnish industry, but usually in a modified form. Rosin has a relatively low melting point; it is easily softened by pressure as well as by heat, and becomes tacky. It can be hardened either by reacting it with zinc or lime to form the metallic resinate, or by esterifying it with glycerin or pentaerythritol, to form ester gum.[9]

The quick-drying or four-hour varnishes were brought about by the combination of synthetic resins with tung oil. Generally speaking, synthetic resins hasten the drying and improve the water and chemical resistance. It is possible, furthermore, to incorporate in a varnish a larger percentage of synthetic resin than of fossil resins. These resins absorb ultraviolet light without alteration, protecting the more sensitive components by their screening effect. The oil-soluble resins are more completely described in Chapter 35.

[9] "Technology and manufacture of hard synthetic coating resins," W. R. Husen, *Paint and Varnish Prod. Manager*, 27, 87 (1947).

The ratio of resin to oil varies with the different types of varnish; in general, the higher the percentage of resin the more brittle and faster-drying the varnish will be. The following classification illustrates the various types and their usage.

"Short"—12-15 gal. oil/100 lbs. resin	for furniture to be rubbed
"Moderately short"—15-25 gal. oil/100 lbs. resin	for many household enamels
"Medium length"—25-35 gal. oil/100 lbs. resin	for spar and floor varnish
"Long oil"—35-50 gal. oil/100 lbs. resin	for durable exterior varnishes

In making a typical varnish the gum resin and the oil are placed in the kettle and heated over the flame of an oil burner set below the floor. The

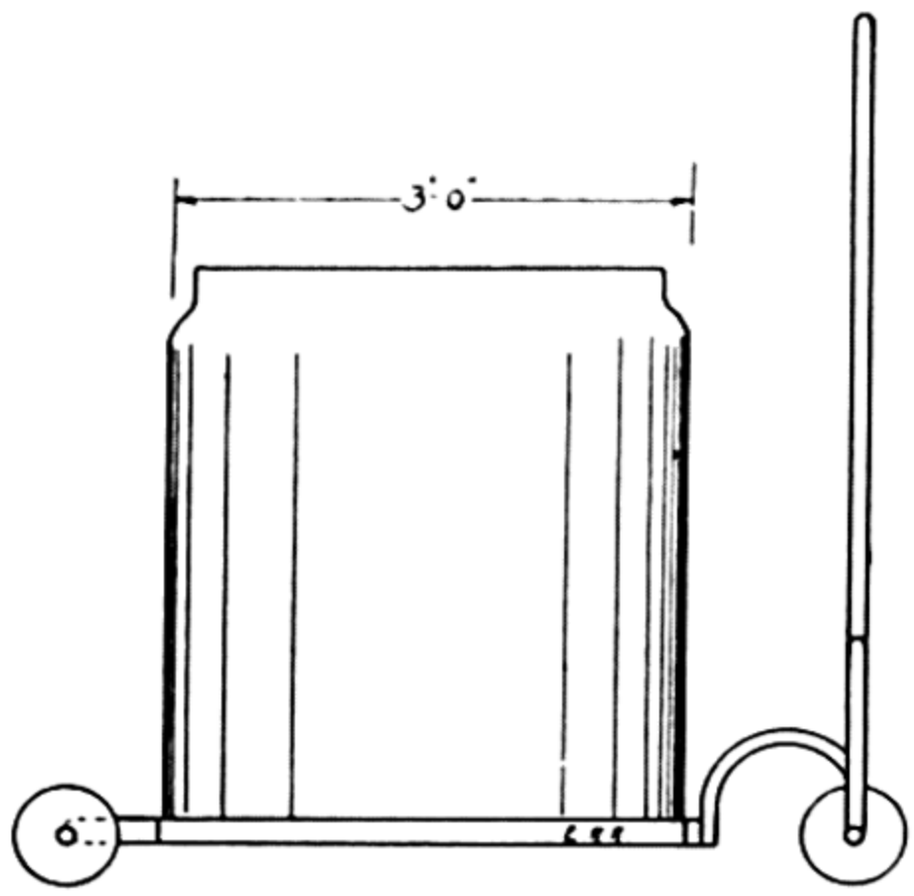


FIGURE 231.—A copper kettle on wheels for varnish-making.

temperature is raised rapidly to 500-600° F. depending upon the product, and is maintained there until the correct body is obtained or until the mixture becomes homogeneous. If driers in the powder form are used, they are added during the cooking process. The kettle is pulled from the fire, cooled and thinned. Liquid driers, such as the metallic naphthenates, are usually added after thinning.

After the varnish is cooled, dirt and foreign material are removed by pumping the varnish through a filter press or centrifuge. The varnish is then pumped into storage tanks. Numerous laboratory tests are conducted to determine specific gravity, viscosity, color, clarity, drying time, water resistance, chemical resistance, baking and elasticity.

The filter press is the more searching device; all clear varnishes are filter-pressed. The centrifuge is more rapid, and is used for varnishes which are to be pigmented into enamels.

Baking japans are varnishes made up with asphaltum instead of resin; the baking is done, for metal surfaces, at 400° F. (204° C.) and lasts 3 to 4 hours. This temperature melts the asphaltum easily, and distributes it evenly; during the baking the oxidation of the oil is rapid, so that on removal of the article the coat is dry. A very beautiful black luster is obtained. By baking at lower temperatures, varnishes containing the usual resins may be used. Such coatings are highly chemical-resistant.

Enamels

Ripple enamel, the attractive enamel seen on the base of many scientific instruments, on metal cases and boxes, is made from an alkyd-resin coating or an oleoresinous varnish of special composition, by baking the coated piece.

Baking has in the past been accomplished by heating the coated article in an electric, gas or steam-heated enclosed oven—a method known as convection baking. Modern production lines, particularly in the automobile industry, are turning toward "baking tunnels" which are lined with infrared lamps and reflectors.[10] Baking tunnel equipment is more costly to install, but it is more efficient.

Enamels, like paints, are pigmented vehicles. The vehicle is usually an oleoresinous varnish; it may, however, also be one of the other coatings which are summarized below. The clear coating is made into an enamel by incorporating pigments. The mixing procedure for preparing an enamel has been described under the procedure for mixing paints.

TABLE 122.—*A classification of clear and pigmented coatings (exterior house paints not included).*

(After O. J. Schultes)

I	II	III	IV
Oleoresinous varnishes and enamels	Alkyd varnishes and enamels	Cellulose clear lacquer and lacquer enamel	Resin lacquers and enamels

I. The oil-resin varnishes and enamels have been fully discussed.

II. The alkyd resins are esters of polyhydric alcohols and polybasic acids. Glyceryl phthalate, its most prominent representative, modified with fatty acids from drying oils, to render it soluble in organic solvents. Most alkyd varnishes are pigmented and serve as enamels.

III. The typical clear lacquer consists of cellulose nitrate, resin (synthetic), plasticizer, solvent and diluent. Here again the pigmented lacquers, called lacquer enamels, make up the bulk of the production.

IV. Dispersions or solutions of resins in organic solvents, often plasticized with oil or chemical plasticizers, are the resin lacquers, and when pigmented, the resin enamels. Several of the new synthetic resins are coming into wide use in resin lacquers: "Vinylite" dissolved in ketones; "Pliolite," in turpentine; "Parlon," a chlorinated rubber hydrocarbon, in toluene and xylene. Spirit varnish belongs in this group, as for example, shellac varnish.[11]

Lacquer enamels are used in large quantities on passenger automobile bodies; they have a nitrocellulose base and belong to class III. The finish used for many other automobile bodies and on truck bodies has an alkyd-resin base and therefore belongs to class II.

[10] "Infrared finishing ovens," Ira J. Barber, *Paint and Varnish Prod. Manager*, 27, 147 (1947).

[11] Intensive study of shellac as to its constitution, and uses, is carried on by "The Indian Lac Research Institute," at Namkum, Ranchi, Bihar and Orissa, India, and is described up to the year 1935 in a handsome book published by the Institute. The outlook for continued, in fact, increased consumption of shellac, partly as a result of these studies, is excellent. In conjunction with laboratories in England, and the Research Institute, work on shellac "splitting," and constitution, is carried on at the Brooklyn Polytechnic Institute.

Lacquers

A lacquer is a protective coating which dries by evaporation of volatile components and whose essential film-forming constituent is a cellulose ester, nitrate, acetate or other, generally combined with a resin. The liquid lacquer applied to the surface to be protected contains, for example: (1) nitrocellulose or nitrated cotton, called "cotton" in the trade; (2) the solvent, usually a mixture of three substances, a ketone, an alcohol and an acetate, such as ethyl. The latter is being replaced frequently by methyl isopropyl ketone, also by methyl ethyl ketone, "Cellosolve" and derivatives; (3) a resin, such as ester gum, dammar, modified phenolics, maleic resin, or an alkyd; (4) the plasticizer, which remains in the film and keeps it flexible; (5) the diluent; (6) a dye or pigment.[12] If the lacquer is to be "clear," no dye or pigment is added. Table 123 shows the ultimate particle size of various pigments used in paints, enamels and lacquers.

Table 123.—*Ultimate particle size of various standard pigments.*

Materials	Maximum residue on No. 325 screen (opening 44 microns) (Per cent)	Average ultimate particle size (Microns)
Carbon black	1.0	0.1
Fine-particle zinc oxide ("Kadox")	..	0.12 to 0.18
Zinc oxide (Florence French process "Green Seal")	1.0	0.21 to 0.26
Lithopone	1.0	0.25* to 0.35
Titanium barium pigment	1.5	...† ...
Zinc sulfide	..	...† ...
High-strength lithopone	..	...† ...
American process zinc oxide	1.0	0.28 0.35
Lamp black	1.0	0.4
High-leaded zinc oxide	1.0	0.35 0.45
Iron oxide (Spanish)	3.0	0.4 0.6
Low-leaded oxide (5% leaded)	1.0	0.50 0.65
Sublimed white lead	1.0	0.65 0.67
Basic carbonate white lead (Old Dutch Process)	1.0	0.75 1.21
Chrome green	2.5	... ...
Ultramarine blue	..	5.0

* According to H. Green, secondary particles (aggregates) of lithopone may be composed of from 2 to 50 ultimate particles. When dispersed the individual particles vary in size from colloids to particles perhaps a half a micron in diameter.

† No definite figures available but approximately the same as lithopone. Table from "Pigments in nitrocellulose lacquer enamels," H. A. Nelson and W. C. Norris, *New Jersey Zinc Co. Research Bull.*, September (1927).

A lacquer coating dries rapidly, by the evaporation of the solvents; the standard varnish dries slowly, partly by evaporation, partly by oxidation and polymerization.

Nitrocellulose, also called pyroxylin, is made by nitrating cotton linters with mixed acid. The nitration is not allowed to proceed as far as when making nitrocellulose for explosives, for the highly nitrated cellulose (12.5 per cent N and over) is not soluble in the selected solvents; for that reason, a "cotton" containing only 11 to 12.4 per cent N is prepared. The linters are purified from oils by boiling with caustic, washed, and if colorless

[12] Formulas for nitrocellulose lacquers will be found on p. 176, *Paint and Varnish Prod. Manager*, 27, (July, 1947).

lacquer is sought, bleached. The nitration is carried out by placing 32 pounds of cotton in 1500 pounds of mixed acid; the great excess of acid is taken to insure negligible change in concentration over the period of nitration due to consumption of nitric acid and production of water.

$$\underset{\textit{cellulose}}{C_{24}H_{40}O_{20}} + 8HNO_3 \rightarrow \underset{\substack{\textit{nitrated cellulose}\\ \textit{or nitrocellulose}}}{C_{24}H_{32}O_{12}(NO_3)_8} + 8H_2O$$

The reaction given here is an ideal one and is meant to indicate the change taking place; a single nitrocellulose is really not formed, but a series of them, with various numbers of nitrate groups in the molecules. The total nitrogen content is the guide.

After 15 minutes in the acid, the cotton is dropped to a centrifuge below, to remove the adhering acid. It is then beaten in pulping machines (8 hours), boiled in poaching tubs (12 hours) with several changes of weakly alkaline waters. Finally the 25 per cent adsorbed moisture is displaced by denatured alcohol forced in under a pressure of 300 pounds. At this stage the nitrocellulose moist with alcohol resembles cotton waste in appearance; it is made in a few plants, and is bought by the lacquer maker who dissolves it and blends it to suit.

Originally the nitrocellulose so made was dissolved in amyl acetate, for example, and articles dipped in the solution. On evaporation of the solvent, a film remained. It was soon observed that only 6 ounces of nitrocellulose could be dissolved in one gallon of the solvent; more gave a solution too viscous to flow. In fact, with 6 ounces, the resulting solution was quite thick. Nitrocellulose which gives rise to such solutions is called *high-viscosity nitrocellulose.* It became desirable to modify the nitrocellulose so that a greater amount of it might be placed in solution, and yet have a solution thin enough to be applicable with a spray gun. Such a modified material is *low-viscosity nitrocellulose,* the manufacture of which is described below. It is now possible to place 24 ounces of nitrocellulose with 16 ounces of additional gums in one gallon of solvent, hence 40 ounces in all of the film-forming material, instead of only 6. The important product now is low-viscosity nitrocellulose. The gums which are suitable additions are dammar, shellac, kauri, rosin ester, etc.

High-viscosity "cotton" is still made, for use in bronzing liquid, and in many lacquer formulas, because the film made from low-viscosity cotton is slightly weaker.

Low-viscosity cotton is produced by heating the first product of nitration with water under pressure. The earlier batch process, in which 4000 pounds of cotton were heated with 60,000 pounds of water, established that during heating, there is a decrease in the nitrogen content from 12.25 to 12.05 per cent nitrogen and that gas is formed. In the continuous process [13] nitrated cotton (1 part) suspended in water (20 parts) is pumped continuously through a 4-inch tube 1000 feet long ending in a 200-foot standpipe. Rate of flow and temperature are controlled, and hence the reduction in viscosity. The resident period is generally 25 minutes. The mixture overflows to tubs,

[18] *Ind. Eng. Chem.*, 22, 326 (1930).

and then passes to centrifugals; the product may be kept moist until called for, or its water may be displaced by alcohol in a dehydrating press, leaving the cotton alcohol-moist. It may be shipped in barrels in that state.

The viscosity depends upon the treatment of the nitrocellulose, as has been stated, but it also depends to some extent upon the solvent. The viscosity of the liquid lacquer can be increased by adding non-solvents such as benzene; it can be reduced by adding such "true solvents" as acetone or ethyl acetate.

Low-viscosity nitrocellulose may also be produced by heating the product of nitration with benzene or ethyl alcohol.[14]

The lacquer is made as follows: the selected resin is dissolved in the diluent; the cotton is dissolved in the solvent, and the resin solution added; solvent or diluent is introduced next, and finally the pigment as a suspension in nitrocellulose solution or in the plasticizer. A tank with agitator is provided.

TABLE 124.—*Production figures for certain varnish and lacquer resins for 1946.**

	Lbs	Per Pound
Alkyd resins, oil type	13,991,000	$0.28
Alkyd resins, modified by rosin ester	36,193,000	0.18
Rosin esters, unmodified	66,569,000	0.15
Rosin-glycerol (ester gum)	41,297,000	0.15
Mixed phenolic resins for protective coatings	12,951,000	0.18

* U. S. Tariff Commission.

The falling-ball method is used for testing the viscosities of lacquers. A steel ball $\frac{5}{16}$ inch in diameter and weighing 2.043 grams is made to fall through exactly 10 inches in a glass tube 14 inches high, 1 inch in diameter, with the liquid tested at 25° C. (77° F.). The time required for the fall is taken with a stop-watch. The concentration of the "cotton" to be tested, and the nature of the solvent must be specified. The specifications suggested by the Hercules Powder Company have been generally accepted: 16 ounces of "cotton" on the dry basis, and as solvent the formula known as No. 366, consisting of ethyl acetate 20, ethyl alcohol 25, toluene 55 parts, all by weight. With the relation given, a solution of a little over 12 per cent nitrocellulose results. In terms of such a solution and of the falling-ball test, a high-viscosity nitrocellulose will require 20 seconds for the fall, while low-viscosity cellulose will be one-half second. Intermediate viscosities are provided.

Plasticizers. By itself, the film of nitrocellulose contracts after the solvents evaporate, so that it wrinkles and buckles away from the surface being coated. This serious defect is successfully counteracted by using in the formula a substance which will not volatilize when the film dries, and hence will remain in the film, and render it plastic. Such substances are castor oil, camphor, diethylphthalate, dibutylphthalate, diamylphthalate, tricresyl phosphate, tributyl phosphate, butyl stearate, and many others. Castor oil is used, if pigments are to be incorporated in the lacquer. By

[14] U. S. Pat. 1,553,494-5.

adding certain substances such as the chlorinated diphenyls, the Aroclors, a decrease in the flammability of the film is secured, in addition to plasticization.

Solvents for Lacquer. The first solvent for nitrocellulose was mixed alcohol and ether; this gave collodion or "new skin." It was improved by the addition of a little castor oil, giving "flexible collodion." For the protective coating, the early solvents were amyl acetate, butyl acetate, and ethyl acetate, the latter two of which are now the most frequently used. The newer solvents are glycol derivatives (Chapter 25), amyl propionate, butyl lactate, cyclohexanol acetate, methylisopropylketone, and many others.

The boiling points of some of the more important solvents are listed below:

Solvent	B. pt. °C.	B. pt. °F.
Ethyl acetate	77	170
Butyl acetate	125	257
Amyl acetate	137	278.6
Cyclohexanol acetate	170	338
"Cellosolve" (Glycol monoethyl ether)	134	273.2

A differentiation between the several solvents is well made in two ways; by the vapor pressure at room temperature,[15] and by the rate of evaporation.[16]

On drying, too volatile a solvent cools the film considerably, so that atmospheric moisture condenses on it; this is called blushing. The remedy is to use a higher-boiling, hence slower evaporating solvent.

Pyroxylin (the mixed nitrocellulose molecules resulting on moderately nitrating cellulose) placed in a solvent and apparently dissolved, gives merely a colloidal solution, not a true solution. A good solvent is one which takes up a large quantity of nitrocellulose, and still remains fairly fluid; a non-solvent takes up none at all. A *diluent* is a non-solvent which is miscible with the solvent; it is added in amounts insufficient to cause precipitation of the nitrocellulose. Toluene, benzene, and petroleum naphthas are diluents.

Cellulose Acetate Lacquer. Cellulose acetate (Chapter 22) as the main film-forming material in the lacquer formula has the great advantage that it is not flammable. Two factors, however, have retarded its wider use; one is that, for a given weight of film-forming material, the viscosity of a solution of acetate is not as low as one of nitrocellulose; the other is the higher cost. The plasticizer is generally tricresyl phosphate.

Uses for Lacquer. There are three main outlets for lacquer which require a tremendous tonnage. First, artificial leather, which is made by coating a cotton fabric with a pyroxylin solution and then embossing to simulate the grain of a leather. Second, the finish for automobile bodies; a nitrocellulose or pyroxylin finish is superior to the standard gum-linseed oil varnish finish in durability, resistance to abrasion, cracking, chalking,

[15] Graph on p. 673, *Ind. Eng. Chem.*, 17, (1926).
[16] Graph on p. 500, *Ind. Eng. Chem.*, 20, (1928).

and in rapidity and ease of application; it is inferior to varnish in luster. The somewhat duller but more durable pyroxylin finish is in turn, however, being replaced by alkyd-type synthetic enamels which are baked on the automobile bodies. Lacquer enamels are finding wider usage for manufactured articles requiring a coating which will air-dry rapidly. Third, interior decoration, woodwork, furniture and the like; here lacquer has the advantage over paint that it dries in less time. The application is mainly by a spray gun; within a few hours the coating is dry. One coating suffices. Brushing lacquers are also prepared and marketed.

Based on figures for November and December 1948, it may be estimated that the Industrial sales of paint and varnish for the year has amounted to $352,025,328, and that of lacquer, to $78,599,178 (Bureau of the Census).

Printing Inks or News Inks

Printing inks should not be compared to ordinary writing inks; in that sense they are not inks at all, but rather paints. They must dry as fast as applied, mainly through penetration into the paper. They are made by mixing carbon black or lamp black with linseed and rosin oils, rosin varnish and a drier.

Rosin oil is used in part, because it is cheaper than linseed oil. It is made by distilling rosin in simple stills, fired by the staves from the rosin barrels; there pass over water, acetic acid, an impure "pinoline," then rosin oil; the residue is pitch, which is run off hot. The rosin oil is refined by a second distillation. Rosin varnish is made by heating rosin till water, acetic acid, and pinoline have passed over, then running all the residual liquid into a mixer containing warm linseed oil. This linseed oil is previously hardened by the following treatment: It is heated in a kettle over an oil burner and when hot enough, flashed, that is, ignited; it is allowed to burn in this way for four hours; then the flame is extinguished by placing a cover over the kettle. Only 5 per cent of the oil is consumed during the burning.

The proper proportions of rosin oil, rosin varnish, and lamp black are mixed in a preliminary way; then this mixture is fed to a number of rather small mills consisting of two horizontal steel disks, of which the upper one rotates on its hollow shaft, and drags the lower one, which is larger, with it but in constantly changing relation. The mixture is fed in from a gallon pail above, through the hollow shaft. The discharge is at the edge by a scraper.

Colored inks for printing are made similarly, using as pigments the metallic compounds of organic dyes as well as inorganic pigments such as Prussian blue and chrome yellow. Some of the organic pigments are Lithol Red, Lake Bordeaux, Helio Fast Red.[17]

The importance of news ink is indicated in the statement that the New York *Herald-Tribune* alone consumes over 4,000,000 pounds of such ink in a year.

[17] "The manufacture of organic dyestuffs," André Wahl, translated from the French by F. W. Atack, London, G. Bell and Sons, 1914, p. 115; also "Printing inks," W. F. Harrison, *J. Chem. Ed.*, 3, 408 (1926).

Other Patents

U. S. Patent 2,033,916, organic phosphates, to impregnate wood, and as plasticizers; 1,848,660, process for the manufacture of a red pigment; 1,981,210, manufacture of a green mineral pigment consisting of cobalt chromite and magnesium orthotitanite; 1,846,188-7, production of white pigments from titanium dioxide; 1,833,087, enamel containing barium and strontium compounds; enamel consisting of white lead, zinc oxide, barium fluoride, chinawood oil, linseed oil, turpentine, gum manila copal, ethyl alcohol and acetic ether; 1,753,616, application of lacquers to metallic surfaces; 1,801,340, nitrocellulose lacquers, and 1,884,255, same, with resins of the coumarone and indene types (*see* Chapter 35); 1,756,100, colored nitrocellulose varnishes; 1,756,267, non-penetrating varnishes and lacquers from reactive resins of the phenol-aldehyde type; 1,817,183, manufacture of lithopone; 1,821,441, paint and enamel with a granulated or powdered base, that can be applied in stippled form; 1,891,079, manufacture of varnish and paint oils, using mixtures of reduced hydrocarbon polymers with varying amounts of drying oils; 1,865,191, a lacquer containing cellulose nitrate, an artificial cyclic ketone resin and a solvent containing at least 20 per cent propylene glycol diethyl ether; 1,826,667-8, piperidine and anisidine as plasticizer in cellulose acetate combinations, *tri-m*-oxyphenyl phosphate as plasticizer and fireproofing agent with cellulose acetate; 1,870,556 (trichloracetamide), 1,836,701 (trimethylene glycol dibutyrate) for similar purposes; 1,836,687, for coating fabrics to form leather substitute; 1,833,136, for making a sheet material of good flatness of hydrolyzed cellulose acetate. U. S. Pat. 2,404,033, cellulose ester-rosin ester composition; 2,404,313, plasticized vinyl resin coating; wrinkle coating from non-conjugated oils, 2,389,794; iron blue pigments for printing inks, 2,392,073.

Problems

1. One ton of lead in the form of buckles is made into white lead having the composition (idealized) $2PbCO_3 \cdot Pb(OH)_2$. If the yield is 95 per cent, how many pounds of white lead will be obtained?

2. With pure materials, what would be the weight of barium sulfate in 1 ton of lithopone?

3. A rouge which analyzes 92 per cent Fe_2O_3, the rest water, is made by heating 5000 pounds of copperas. How much rouge is obtained?

Reading References

"Scientific aspect of paint technology," L. A. Jordan, *J. Soc. Chem. Ind.*, **48**, 13T (1929).

For zinc oxide, read in "Metallurgy of zinc and cadmium," by H. O. Hofman, pp. 285-301; New York, McGraw-Hill Book Co., 1922.

"The glycol ethers and their use in the lacquer industry," J. C. Davidson, *Ind. Eng. Chem.*, **18**, 669 (1926).

Eight articles on the subject of protective coating will be found in *Ind. Eng. Chem.*, **19**, 968-985 (1927).

"Articles on lacquers and solvents," *Ind. Eng. Chem.*, **20**, 183-200 (1928).

"The manufacture of nitrocellulose lacquers," R. G. Daniels, London, Leonard Hill, Ltd., 1933.

"Manufacture and use of lacquers, a lecture," Dr. L. A. Pratt, *Am. Paint J.*, **17**, No. 3, p. 52, Oct. 31, 1932.

"The development of Duco type lacquers," M. J. Callahan, *J. Soc. Chem. Ind.*, **47**, 232T (1928).

"Phenol resinoids in oil varnishes," V. H. Turkington, R. C. Shuey and W. H. Butler, *Ind. Eng. Chem.*, **22**, 1177 (1930).

"Service requirements of insulating varnishes," R. H. Arnold and L. E. Frost, *Ind. Eng. Chem.*, **25**, 133 (1933).

"The newer chemistry of coatings," Carleton Ellis, *Ind. Eng. Chem.*, **25**, 125 (1933).

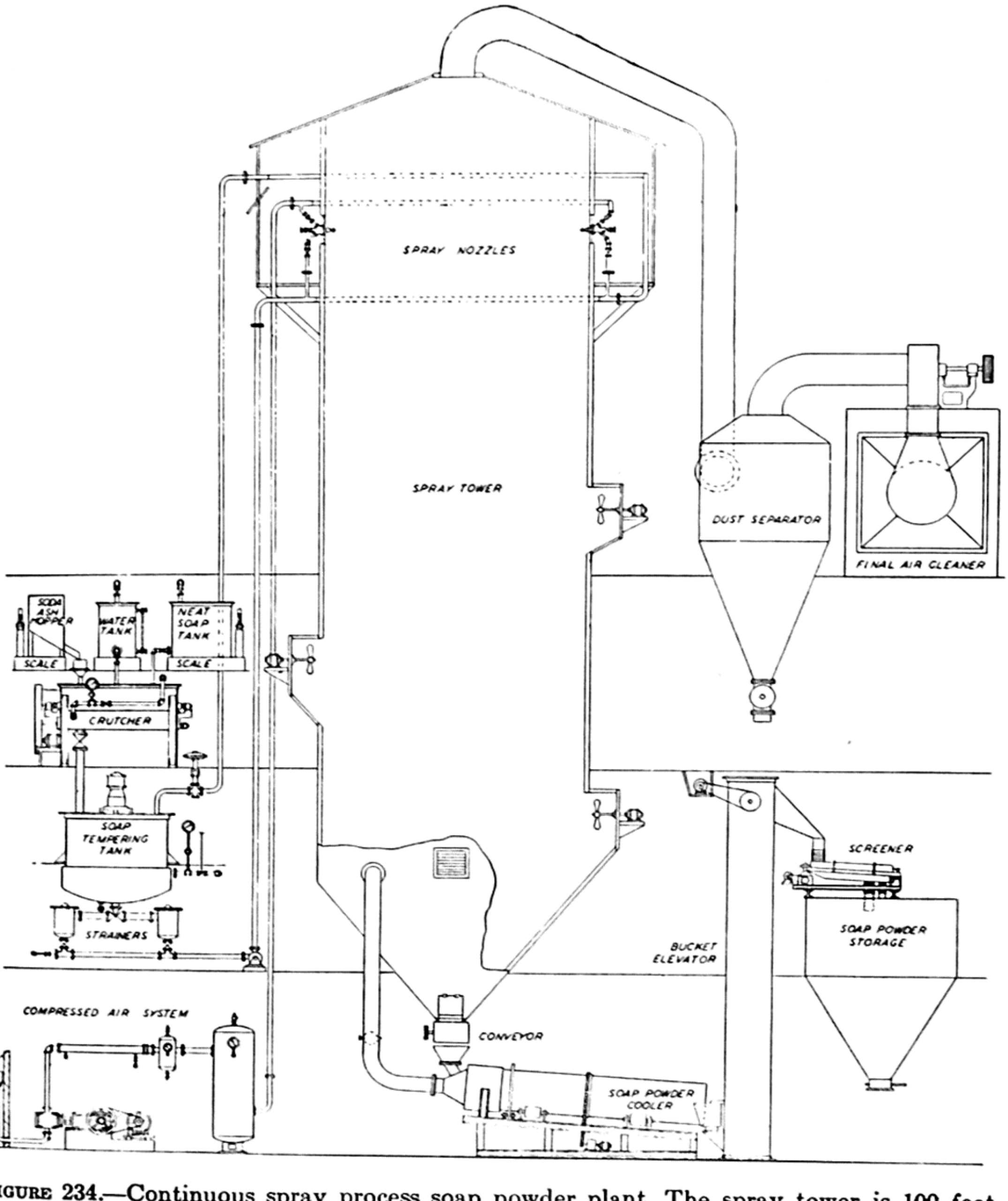


FIGURE 234.—Continuous spray process soap powder plant. The spray tower is 100 feet high. (Courtesy of Wurster and Sanger, Inc., Chicago, Ill.)

cent) in open, lead-lined wooden tanks. The catalyst is made by sulfonating a mixture of oleic or other fatty acid and naphthalene.[8] The melted fatty acids produced are washed free of acid with water, and used as such or are refined by distillation at very low pressures, supplemented by crystallization from solvents. The acid waters are treated with lime, filter-pressed to remove the calcium sulfate, and the clear filtrate distilled for its glycerin.

[8] U. S. Pat. 601,603 (1897).

Hydrolysis of Glycerides

The hydrolysis of glycerides by means of water only, at higher temperatures and higher pressures, has been carried out in batch processes,[9] with metallic oxides as catalysts; this is now a continuous process,[10] without any catalyst. In the continuous process, the time required is very short (two hours or less), contrasted with 6 to 10 hours for the batch process, and 30 to 40 hours for the Twitchell process. The temperature is held at about 485° F., and the pressure high enough to prevent the water from vaporizing (700 lbs./sq. in.), for the reaction is between liquid water and liquid glycerides.

The equipment is shown in Figure 235; its essential part is the hydrolysis tower, down which preheated water travels, and up which the fatty acids formed by the hydrolysis rise. The tower in the pilot plant is 5 inches in diameter and 42 feet high, and is fitted with numerous trays. The trays in the upper part have one riser and one downspout; those in the lower part are perforated, and carry one riser for the fatty phase. Good contacting of the two layers is thus assured. The oil-water ratio usually is 1.6 to 1. The glyceride is fed in near the bottom of the tower; the fatty acids leave at the top, comparatively cool. They may be purified by heating to 445° F., for example, and flash-distilled, at a pressure of 4 millimeters Hg. A water solution of glycerin containing 10 to 25 per cent of the latter leaves at the bottom of the still, comparatively pure, so that its concentration offers no major difficulties. The overall yield by this process is 96 to 99 per cent. The hydrolysis reaction may be represented as follows:

$$(C_{17}H_{35}COO)_3 \cdot C_3H_5 + 3H_2O \rightarrow 3C_{17}H_{35}COOH + C_3H_5(OH)_3$$

a fat — *fatty acid* — *glycerin*

Another process for liberating the glycerin is the lime soap process, which has been used in Europe to some extent.

To the fatty acids from greases and glyceride oils there have been added within the past several years fatty acids obtained from tall oil, a by-product of the wood-pulp industry. This ill-smelling, low-grade raw material is separated by fractional distillation at low pressure into a fatty acid fraction, a rosin acid fraction, and a light-colored pitch as residue. The first fraction may be used as such (88 per cent oleic-linoleic acids), or it may be redistilled to give a product with 94 per cent oleic-linoleic acid ("Neo-Fat D-142").[11]

Purification by fractional distillation under vacuum and redistillation is supplemented by separation by means of solvents, which may involve a crystallization. In the Emersol process,[12] the distilled fatty acid mixture is dis-

[9] U. S. Pat. 2,154,835, the Eisenlohr process.

[10] "Continuous hydrolysis of fats," H. D. Allen, W. A. Kline, E. A. Lawrence, C. J. Arrowsmith and C. Marsel, *Chem. Eng. Progress*, 43, 459 (1947); see also U. S. Pat. 2,267,750, Reissue 22,006, on the hydrolysis of fats and oils, to the late Dr. Martin H. Ittner; 2,387,884, on process for hydrolizing fats; and 2,156,863, to Victor Mills.

[11] *Chem. Industries*, p. 247 (1949). See also "The selection and uses of fatty acids," "The chemistry of fatty acids," articles publ. by Armour Chemical Division in pamphlet form, 1355 W. 31, Chicago 9, Ill.

[12] See booklet under that name by Blaw-Knox Co., Pittsburgh, Pa.; also *Ind. Eng. Chem.*, 39, 126 (1947).

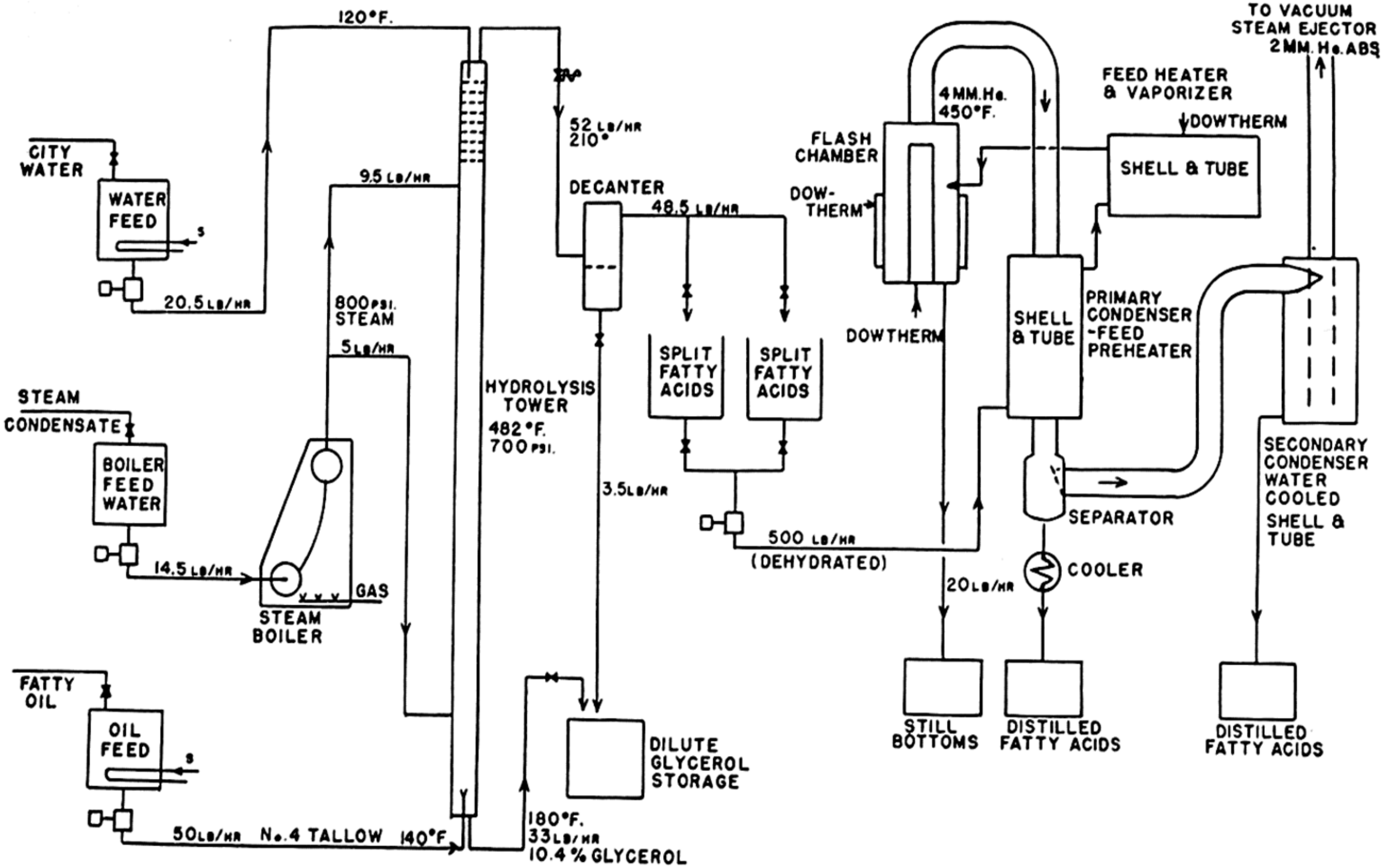
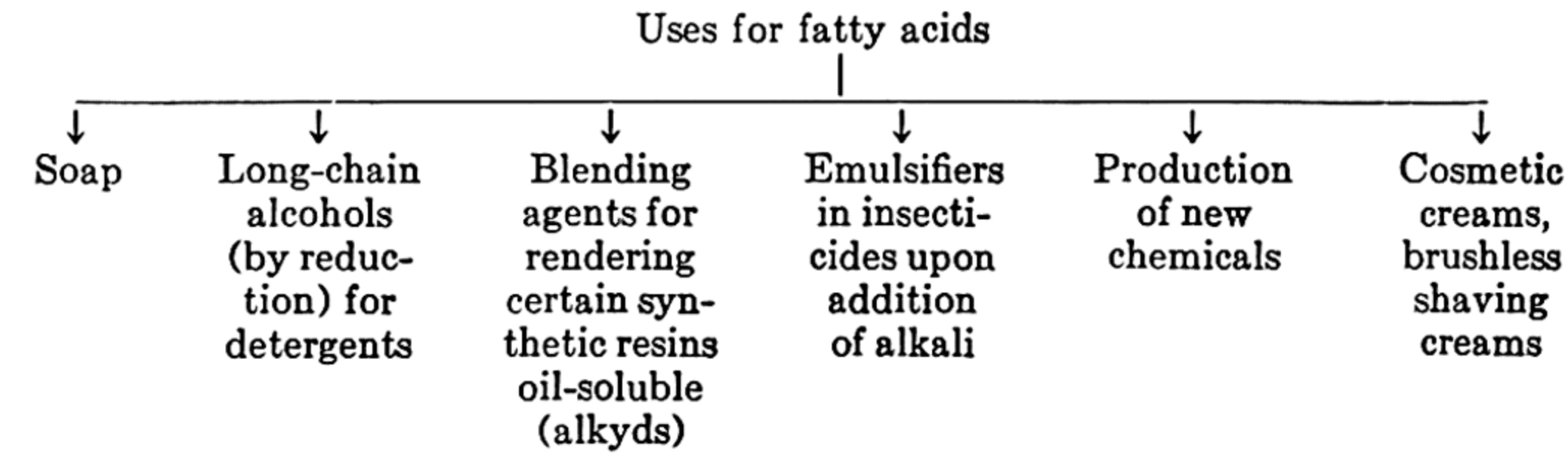


FIGURE 235.—Flow diagram for the continuous hydrolysis of glycerides by water alone. [*Chem. Eng. Progress*, 43, 459 (1947).]

solved in methyl alcohol and the solution chilled in a multi-tubular crystallizer, causing the formation of stearic acid crystals, for example, leaving oleic acid in the solvent (again for example). The crystals are separated on a rotary vacuum filter, washed with cold alcohol on the filter, then melted and passed to a still where the solvent is driven off, leaving the pure fatty acid as finished product. A similar treatment yields a finished oleic acid.

Stearic acid may be cast into cakes or fed to a flaker. Powdered stearic acid may be made by atomizing the molten acid at the top of a spray tower.

The fatty acid in any glyceride, animal or vegetable,[13] may be obtained in the free state by boiling with a caustic solution, forming the sodium soap, and treating the latter with sulfuric acid of medium strength; after good mixing, the warm fatty acid floats as an oil over the acidulated water and may be run off. The composition of the fatty acids vary; so also do their physical state,[14] their cost, and their uses. The latter have increased rapidly, as indicated in the following chart.



The development of the fatty acids industry is indicated by the following production figures.

TABLE 126.—*Production of fatty acids in the United States (1946).**

	Pounds
Vegetable oil fatty acids, including fatty acids from tall oil	191,748,000
Fish and marine mammal fatty acids	33,421,000
Animal fat and oil fatty acids	249,135,000
Tall oil, refined	35,646,000†

* Bureau of the Census.
† 1947.

Soap-Making with Fatty Acids

The fatty acids to be made into soap are neutralized with the proper equivalent of caustic in the form of a solution of definite water content. Salt is added (in small amount), and several batches are blended at 200° F. The soap then goes to crutchers, or to equipment for milled soap, or for flake soap, or to a spray-drying tower. Additions of builders are made in the proper places. In the modern plant,[15] a floating toilet soap is made by

[13] It is interesting to note that all the naturally occurring fatty acids have an even number of carbon atoms, which form a straight chain.

[14] After cooling, the free fatty acids in castor oil form a liquid, those in cocoa butter, a solid, those in tung oil, a soft solid, those in coconut oil, a solid overlaid by a liquid.

[15] "Continuous process for soap," Gordon W. McBride, *Chem. Eng.*, p. 94 (April, 1947).

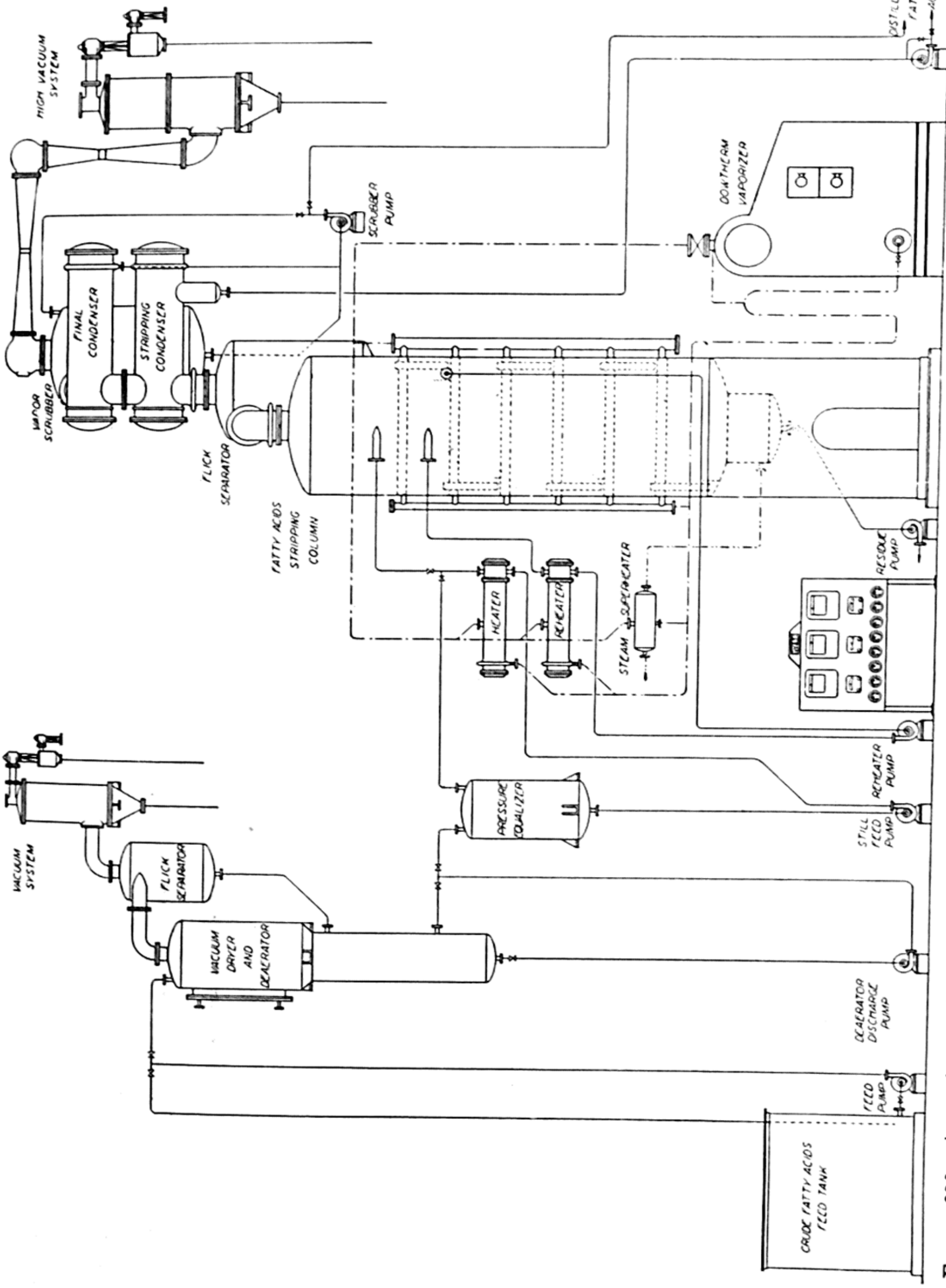


FIGURE 236.—A continuous fatty acid distillation plant with high vacuum. (Courtesy of Wurster and Sanger, Inc., Chicago, Ill.)

heating the soap to 400° F. under a pressure of 700 lbs/sq in., then flashing, reducing the temperature to 220° F., at which the soap is a viscous, pasty mass, with 20 per cent water. It is cooled further in special machines (Votator), where air is introduced during cooling. The soap is fed to an extruder which delivers a strip moving at a rapid rate. The strip is cut into 3-bar lengths and cooled further so as to be no longer sticky; then it is cut to size, embossed and wrapped. The time from fat to finished soap is reduced to one day, as contrasted to the two weeks required in the traditional kettle process.

In 1947, soapmakers produced between 3.6 and 4 billion pounds of soaps of all kinds; the estimate for 1948 is still higher, in addition to a separate total of 700 million pounds of detergents.

Glycerin

Crude Glycerin. The spent lye drawn from the kettle in the boiled process contains the glycerin (5 per cent), the salt (10 per cent), some albuminous substances, free alkali, and soap in solution. The alkali content is normally 0.4 per cent or less; for purification, aluminum sulfate is added; there are formed aluminum hydroxide and aluminum soaps, both insoluble. This precipitate settles well in the slightly acid solution; it is filter-pressed, and the filtrate made slightly alkaline before concentration. (*See* Fig. 237.) The concentration is performed in a closed, upright cylindrical steel vessel with conical bottom, and fitted with a steam chest. The steam in the coils is low-pressure, 5 to 25 pounds; this is sufficient because the pressure on the liquid is reduced by a vacuum-producing device, usually a steam jet ejector, to well below atmospheric. Water vapor passes out, and when the specific gravity of the liquid has reached 29° Bé., the salt can no longer be held in solution, and separates, dropping into the cone. The whole content of the evaporator is dropped into the salt box, a box with a false bottom covered with a filter screen; in this salt box, the salt settles on the screen. The clear liquor is sucked from below the screen into the still; glycerin water from the soap kettle is run onto the salt, this suspension settled again and the liquor also sucked into the still. The salt, now fairly free from glycerin, is blown with steam, and then discharged by hand labor; it still retains 0.5 per cent of glycerin or so, but this is not lost, for the salt is used over again in the kettle room.

The liquid drawn back into the still from the salt box is much lower in specific gravity, for it has lost the salt; its glycerin content is about 49 per cent. The evaporation is continued until 80 per cent is reached, and the red liquid then obtained is the "soap lye crude glycerin" of commerce. The test for this stage consists of heating a small sample in an open dish, when a boiling point of 158° to 160° C. must be reached.

When the salt drum is used, the salt is allowed to collect in the drum as it forms, until the drum is filled with a salt sludge consisting of salt in the thickened glycerin. The sludge is then blown into a hopper from which it drops to centrifugals; the glycerin is returned to the evaporator, the salt washed with a little water and discharged. In this operation the

salt drum functions as a blow case. A rotary drum suction filter may replace the centrifugal.

There is a second kind of crude glycerin, called "saponification crude," produced by concentrating the glycerin waters from the catalytic, the batch pressure (the autoclave), or the continuous-pressure process for fat hydrolysis. Soap lye crude contains 80 per cent glycerin; saponification crude, 88 per cent.

Crude glycerin is the raw material of the glycerin distillers, a separate enterprise. Many large soapmakers, however, distill the glycerin in their own plants.

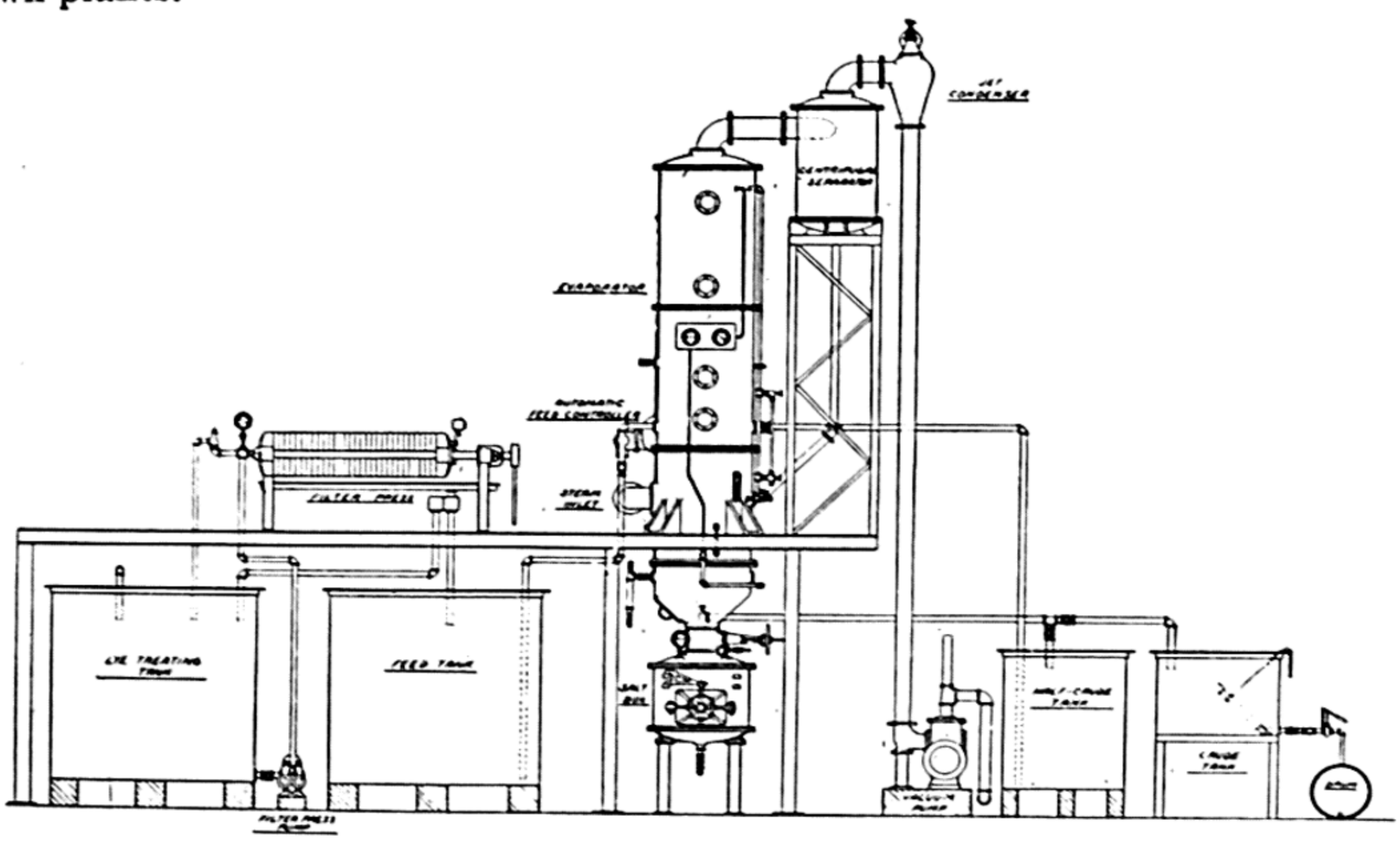


FIGURE 237.—Spent soap-lye glycerin treating and evaporating plant. Steam chest in evaporator not shown. Note salt box under evaporator. (Courtesy of Wurster and Sanger, Inc., Chicago, Illinois.)

Purification of Crude Glycerin. The crude glycerin with a red color is refined to a purer, straw-colored glycerin by distilling it under reduced pressure in a current of steam. The earlier batch stills have been replaced by stills with continuous operation. By reducing the pressure to 6 to 12 millimeters Hg (absolute), the distillation takes place with the liquid at a temperature of 315 to 320° F. (157-160° C.) at which comparatively low temperature no decomposition takes place. About 0.25 pound of steam is injected per pound of glycerin distilled. The steam economy is important; in recently constructed units,[16] the overall steam consumption, for the heating coil, vacuum producers, glycerin discharge pump, and injected steam, is held to 2½ to 3½ pounds per pound of glycerin distilled. The steam and glycerin vapors pass to three heat exchangers in series. The first two are held at temperatures high enough to permit the steam to pass, but cool enough to condense most of the glycerin. The vapors reach the third cooler, the

[16] "Glycerin refining plants," Oscar H. Wurster (Wurster and Sanger, Inc., Chicago, Ill.), with two flowsheets.

condenser, where the remaining glycerin with a little water is condensed to give a 90 per cent glycerin, which is concentrated further to dynamite glycerin. The balance of the steam is ejected. The condensates in the first two coolers enter a deodorizing unit, after leaving which they are of high enough grade and strength to serve as commercial distilled glycerin without additional operation. The glycerin-salt slurry which forms in the crude still is filtered, and its salt is re-used, while the filtrate is distilled for its glycerin in the foots still, at low pressure. The total recovery in the refining operation is 97 to 98 per cent.

The traditional procedure applies primarily to glycerin obtained in the kettle (or boiled) process. The procedure is modified for the purer product obtained by the continuous-pressure process.

A considerable amount of distilled glycerin is made into dynamite glycerin, by concentrating it again at reduced pressure, pulling away the water vapors until the content of glycerin is 99.8 to 99.9 per cent, and the specific gravity 1.262 at 15° C. Dynamite glycerin is straw-colored.

The distilled glycerin is made into the U.S.P. grade by treating it while lukewarm with bone char, filtering, and redistilling the filtrate in a separate still used for nothing else. The distillate is treated with bone char a second time, filtered, and is then as white as distilled water. It has a strength of about 98 per cent, and a specific gravity of 1.258 at 15° C.

The yield of glycerin as dynamite glycerin or U.S.P. glycerin is about 90 per cent of the glycerin contained in the solution from the soap kettle.

Synthetic Glycerin. Since mid-1948, a large-scale plant has been producing synthetic glycerin by synthesis, an achievement preceded by some 10 years of intense study and experimentation.[17] This takes its place on the growing list of petrochemicals, inasmuch as it is made from propylene, a petroleum hydrocarbon. The success of the synthesis was practically assured with the discovery that allyl chloride could be produced by the hot chlorination (at 500° C.) of propylene; one hydrogen of the methyl group may be substituted by the chlorine without affecting the double bond:

$$\underset{\textit{propylene}\ \text{(a gas)}}{CH_2{:}CH\cdot CH_3} + Cl_2 \rightarrow \underset{\textit{allyl chloride}\ \text{(b.p. 44.9° C.)}}{CH_2{:}CH\cdot CH_2Cl} + HCl$$

Allyl chloride may be reacted with chlorine at lower temperatures, or with hypochorous acid, and the product readily hydrolyzed to give glycerin.

$$\underset{\textit{allyl chloride}}{CH_2{:}CH\cdot CH_2Cl} + HOCl \rightarrow \underset{\textit{chloroglycerolchlorhydrin}}{CH_2OH\cdot CHCl\cdot CH_2Cl}$$

$$CH_2OH\cdot CHCl\cdot CH_2Cl + 2NaOH \rightarrow \underset{\textit{glycerin}\ \text{(a liquid)}\ \text{(b.p. 290° C.)}}{CH_2OH\cdot CHOH\cdot CH_2OH} + 2NaCl$$

In practice, allyl chloride, purified of HCl and twice distilled, is reacted with chlorine, caustic soda and water, under controlled conditions, to give a

[17] "Commercial scale manufacture of allyl chloride and allyl alcohol from propylene," A. W. Fairbairn, H. A. Cheney and A. J. Cherniavsky, *Chem. Eng. Progress*, **43**, 280 (1947). Same journal, News section, Oct. 1948, p. 16. "Synthetic glycerol from petroleum," E. C. Williams, *Tr. Am. Inst. Chem. Eng.*, **37**, 157 (1941). "Synthetic glycerin from petroleum," E. C. Williams, *Chem. Met. Eng.*, **47**, 834 (1940).

dilute solution of glycerin and salt. The solution is treated not unlike the similar solution of natural glycerin, already described. To produce the allyl chloride, chlorine and preheated propylene are fed to a reactor, where the reaction heat added to the preheat produces a temperature of 500° C., at which temperature the substances react in seconds. Side reactions are few and limited. The vapors leaving the reactor are cooled and treated as follows: the hydrogen chloride is removed by water scrubbing; the allyl chloride and small amounts of other organic chlorides are absorbed in kerosine; the gas leaving the second absorber is unchanged propylene, and this is stored and recycled. The kerosine solution is fractionated, giving the allyl chloride fraction among others.[17a]

Allyl chloride serves, moreover, for the production of allyl alcohol, useful in many ways, *e.g.*, for the manufacture of allyl phthalate and allyl acrylate, used in the preparation of synthetic resins.

Earlier efforts to produce glycerin artificially involved the fermentation of sugar under specified conditions.[18]

Glycerin is used not only in dynamite manufacture, but for many other purposes: in paper making, in the manufacture of cellophane, in certain inks; as part of the fluid in hydraulic brakes for airplanes and automobiles, and in many shock absorbers. The U.S.P. grade is used in pharmacy and in cosmetics. Glycerin is valuable as a solvent, a wetting agent, and as material for the manufacture of certain chemicals. In spite of the competition of newer synthetic chemicals, the uses for glycerin are still expanding.

The production of crude (80 per cent) glycerin in the United States in 1947 was 207,768,000 pounds, on the 100 per cent glycerin basis; in addition, 91,388,000 pounds of dynamite glycerin and 99,765,000 pounds of U.S.P. glycerin, both on the 100 per cent basis, were produced. In 1948, the production of crude glycerin was 195,968,000 lbs. It must be presumed that the glycerin reported here is essentially all natural glycerin; the synthetic glycerin production will make itself felt in subsequent years.

The quotation for 80 per cent crude glycerin is 27 cents a pound; for the dynamite grade, 40 cents, for the U.S.P. grade 40 to 42 cents (Dec., 1948).

Synthetic Detergents

The commercial "synthetic detergents" were devised originally as improved wetting agents for textiles about to be dyed. They were developed further to provide chemicals which would have all the virtues of soap and none of its defects. Soap is an excellent detergent, but in hard water, it precipitates calcium and magnesium soaps; in acid solution soap is decomposed and precipitates its free acid. Among the 125 surface-active agents recently listed[19] there are true detergents (dirt removers), and wetting,

[17a] "World's first synthetic glycerol plant," P. W. Sherwood, *Can. Chem. Process Ind.*, 32, 1102 (1948).

[18] "U. S. Pat. 1,511,754; 1,551,997; read also "Purification of glycerol by crystallization," H. B. Hass and J. A. Patterson, *Ind. Eng. Chem.*, 33, 615 (1941).

[19] "Synthetic Detergents," John W. McCutcheon, *Chem. Industries*, 61, 811 (1947), contains a list of 400 commercial names for surface-active agents, many of which are varying mixtures and modifications of the same agent. See also an earlier list by F. J. Van Antwerpen, *Ind. Eng. Chem.*, 33, 16-22 (1941), repeated with alteration in the same journal, 35, 126-130 (1943).

foaming, penetrating, dispersing and emulsifying compounds. Generally, a given agent excels in one of these functions, but is capable of exercising several. A number of types of synthetic detergents may be distinguished. Soap itself is excluded, mainly for the sake of clarity, and because its production makes it a giant.

An example of the alkyl aryl sulfonate type is "Nacconol NR"; another is "Santomerse 1." The former is a white powder, the sodium salt of a benzene sulfonate which has a long aliphatic side chain attached to the benzene nucleus. It is made as follows: [20]

A mixture of aliphatic hydrocarbons, preferably with 12 to 16 carbon atoms and therefore of the kerosine type, is chlorinated; after purification, the chlorinated hydrocarbon is combined with benzene with the aid of aluminum chloride (the Friedel-Crafts reaction), with elimination of hydrogen chloride. The alkylate is purified by distillation and sulfonated, preferably with one sulfonic group in the molecule. The sulfonated product and any residual acid are neutralized with soda ash, yielding sodium alkyl benzene sulfonate and sodium sulfate. The content of sodium sulfate is adjusted by addition of selected salt cake to reach 55 to 65 per cent of the total solids. The solution is dried on drum driers, to produce powders and flakes, of which "Swerl" is an example, or in spray driers to form uniform globular white particles.

The product is an excellent detergent, not only in warm water (as soap is), but also in cold water; moreover, its cleansing action is rapid, while that of soap is slow. It is effective in waters with 300 ppm hardness and less. The sodium sulfate is a diluent, but it also improves the washing function. "Nacconol NR" is effective in strong acids. "Nacconols" and other alkyl aryl sulfonates are likewise useful in non-aqueous mediums; they clean in a dry cleaner's solvent much as soap does in water.

A second group is comprised of long-chain (C_8 to C_{18}) alcohol sulfates of which "Gardinols," and "Duponol WA" [$CH_3(CH_2)_{10}\cdot CH_2\cdot OSO_3Na$], are examples. The alcohols are produced by the high-pressure catalytic hydrogenation of natural oils with a copper-chromium oxide catalyst, or by low-pressure reduction with sodium hydride. Other examples are "Merpol," "Alrosene PD," and "Avitex C," all white solids in powder or granule form. The compounds of this type are compatible with soap, stable in acid as well as in alkaline solutions, and effective in water with as much as 2500 ppm hardness. Both these and the alkyl aryl sulfonate type are anionic-active; they form a large anion, in contrast to the cation consisting of Na^+, or of K^+, if the potassium salt has been produced.

Still another type are the quaternary ammonium compounds, such as trimethyl cetyl ammonium chloride, which forms in water solution a large cation (carrying the positive charge), with only the chloride ion in the negative part. The compounds in this class are cationic-active agents. Other examples are "Triton X-400," "Agent M," "Alsorept," and all mainly wetting and foaming agents, active in acid or neutral solutions. They are not compatible with soap, nor with anionic-active synthetic detergents.

[20] U. S. Patents 2,364,767 and 2,393,526.

A fourth type is the sulfonated amide, and a fifth one the sulfated and sulfonated esters.

Besides anionic-active and cationic-active (surface-active) agents, of which examples have been pointed out, there are non-ionic agents, of which one example is diethyleneglycol stearate.

The alkyl aryl sulfonates have the great advantage of being relatively cheap, 40 to 45 cents a pound for the 100 per cent activity material; they account for about half the production of synthetic detergents. The long-chain alcohol sulfates are superior in several respects to the alkyl aryl sulfonates, but they cost more (75 to 90 cents a pound), and this restricts their use. Further, they require the fatty glycerides which serves also for making soap, so that in a period when soap is short for lack of oils, the long-chain alcohol sulfates may not be available to replace soap. The alkyl aryl sulfonates depend on petroleum, of which there is an abundance. About 20 per cent of the total production is of the long-chain alcohol sulfate type. The quaternary ammonium compound type accounts for about 2 per cent of the total production; their cost is about $1.29 a pound.[21]

Synthetic detergents have found many uses, in addition to the more evident ones. A dilute solution has been found superior to clean broccoli; it is added to advantage to oil-well drilling mud; a cationic-active agent is used in the viscose coagulating bath to help keep the openings in the spinnerets clean.

In 1947, the United States production of surface-active agents was 290,692,000 lbs, including 38,448,000 lbs of sulfonated oils such as castor. The difference, 252,244,000 lbs, is for 100 per cent activity material. On the basis of 33 per cent activity, the figure becomes three times as great. The overall price is given as 0.26 cents per pound.[22]

Other Patents

1,853,807, on manufacture of resinous soaps; 1,887,743, transparent or opaque toilet soaps and medicated soaps; 1,874,388, rapid, continuous process and apparatus for making soap, intended to replace the cold process; 1,885,166, distillation of glycerin by injecting superheated steam; 1,837,010, production of pure glycerin. U. S. Pat. 2,400,859, glycerol by fermentation; 2,386,381, producing glycerol; 1,936,497 and Brit. Pat. 410,782, on purification of glycerol. U. S. Pat. 2,411,435, on wetting agent.

Problems

1. A soap powder is to be made from a soap solution containing 20 per cent soap and 40 per cent sodium carbonate. Let all of the sodium carbonate be transformed into crystals of the monohydrate, and let the soap retain 5 per cent moisture. How much water will have to be lost by evaporation in order to reach apparent dryness of the powder?

2. Let saponification reaction take place as stated in the introduction to the chapter, in the first reaction, with a fat. If 1200 pounds of NaOH (100 per cent) are consumed, how many pounds of glycerin are produced? If the caustic is in the form of 18° Bé. solution with 12.6 per cent NaOH, and the kettle has three times the capacity of the caustic solution, what would be the necessary size in cubic feet? Select dimensions which will reflect the shape of kettle shown in the illustration in the text.

[21] "Synthetic Detergents," John W. McCutcheon, *Chem. Industries,* 61, 811 (1947).
[22] United States Tariff Commission, 1947 Preliminary Report.

Reading References

"Soap-making manual," E. G. Thomssen, New York, D. Van Nostrand Co., 1922.

"Modern soap and detergent industry," G. Martin, London, Crosby Lockwood & Son, 1932.

"American soap makers' guide," B. P. Meerbott and I. V. S. Stanislaus, New York, Henry Carey Baird & Co., 1928.

"Moderne Toileten Seifen," Julius Schaal, Augsburg, Verlag Ziolwski.

"Middle soap," R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, 24, 1329 (1932).

"Effect of p_H on action of soap," F. H. Rhodes and C. H. Bascom, *Ind. Eng. Chem.*, 23, 778 (1931).

"Synthetic glycerin from petroleum," E. C. Williams and associates, *Chem. Met. Eng.*, 47, 834 (1940).

"Economic aspects of synthetic glycerin production," E. C. Williams and associates, *Chem. Met. Eng.*, 48, 87 (1941).

"Glycerin distillation," Oscar H. Wurster, Amer. Oil Chemists' Soc. Chicago meeting, October 6-7, 1938.

"Processing oils and fats," Oscar H. Wurster and Gervase J. Stockmann, an outline in book form of the processes of refining, bleaching, hydrogenating and winterizing, and the manufacture of salad oil, cooking oil, shortening and ghee from vegetable oils; Chicago, Wurster and Sanger, Inc., Second edition, 1941.

"Recovery of crude glycerin," Oscar H. Wurster, *Oil and Soap,* 13, 246-253, 283-286 (1936).

"Synthetic organic chemicals from petroleum, an American development," Benjamin T. Brooks, *Ind. Eng. Chem.*, 31, 515 (1939).

"The chemical constitution of the natural fats," T. P. Hilditch, London, 1940. "The industrial chemistry of the fats and waxes," T. P. Hilditch, London, 1927.

"The fats and oils, a general view," Carl L. Alsberg and Alonzo E. Taylor, Stanford University, Food Research Institute, 1928.

"Soapmaking in wartime," by Dr. E. G. Thomsen, The Givaudanian, Sept. 1944, p. 3.

"Cleaning up the world, the story of soap," *Oilways,* July 1948.

"Fatty acids and their derivatives," A. W. Ralston, New York, John Wiley and Sons, 1948.

"Chemicals from fats," A. W. Ralston, *Chem. Eng. News,* 25, 836 (1947).

While the atomic bomb holds the center of the stage of world affairs, literally dozens of types of chemical explosives perform their labor-saving tasks in everyday industry. They do their work faster, more cheaply, and with more effectiveness than is possible by any other means. Other chemical explosives are held ready to serve the military forces, should the need arise.

Chapter 33*

Chemical Explosives

Explosives serve two main purposes. In industry, the latent energy of the explosive is utilized to save billions of man-hours of work each year, not only in dislodging rocks, clearing land, blasting ditches, and mining coal and other minerals, but in such small devices as blind rivets and starter cartridges for aircraft and Diesel engines. The other major use is in ammunition, not only for war but also for sporting purposes; and in all other explosive munitions, such as aerial bombs, rockets, torpedoes, grenades and mines. The manufacture of explosives in peacetime is a considerable industry; in 1941, the several plants in the United States turned out nearly 500 million pounds of industrial explosives. In his excellent compilation,[1] Bebie lists some 135 chemicals and formulations which are useful as explosives; of these, about 75 are used by industry alone, 45 are primarily military explosives, and 15 are used for both purposes.

An explosive is a chemical substance or mixture of substances which, when subjected to heat, percussion, detonation, catalysis or friction, undergoes a very rapid transformation with the evolution of a large amount of heat and a volume of gases considerably greater than the original volume of the explosive substance. When this change takes place in a confined space, an extremely high pressure is developed which will shatter the confining walls, or if developed at a relatively slower, controlled rate, may be used to propel a projectile. The various explosives differ not only in sensitivity to shock, or the ease with which detonation can be started, but also in the rate of propagation of detonation or burning throughout the mass of explosive (brisance), and the expanded volume of hot gases produced (strength). The uses to which the explosive is put depend upon all three characteristics, and these are the basis for the grouping used in Table 127.

The velocity of detonation or explosion is determined by the method of Dautriche. A tube filled with the sample is fitted with two auxiliary detonators, which are set off when the explosion passes them; each is connected to a standard trinitrotoluene fuse (copper pipe) which terminates at a thick sheet of lead ($3'' \times 15'' \times \frac{1}{2}''$) as indicated in Figure 238. Each fuse, on burning, causes a bend in the sheet; the position of the point where the two bends meet relative to E is the measure of the velocity.

The usual classification of explosives is into two general groups, *high explosives*, and *low* or *progressive explosives*. The low explosives have the

* In collaboration with A. Robert Fowler, Chemical Engineer, Niagara Falls, N. Y.

[1] "Manual of Explosives, Military Pyrotechnics and Chemical Warfare Agents," Jules Bebie, New York, The Macmillan Co., 1943.

slower propagation rate and, on burning, provide a powerful pushing effect; they are used as propellants. With high explosives, the detonation shock wave passes so quickly (almost instantaneously) through the mass that a great shattering effect results. Some high explosives are so sensitive that they are unsatisfactory as a bursting charge; these are the *initiators* (sometimes called "detonators"), which are used in very small quantities to initiate the detonation or burning of other explosives. Others such as tetryl and PETN are borderline cases, quite sensitive, but still suitable for use by themselves as the bursting charge in small-caliber ammunition if proper precautions are observed; however, these commonly are used as a small

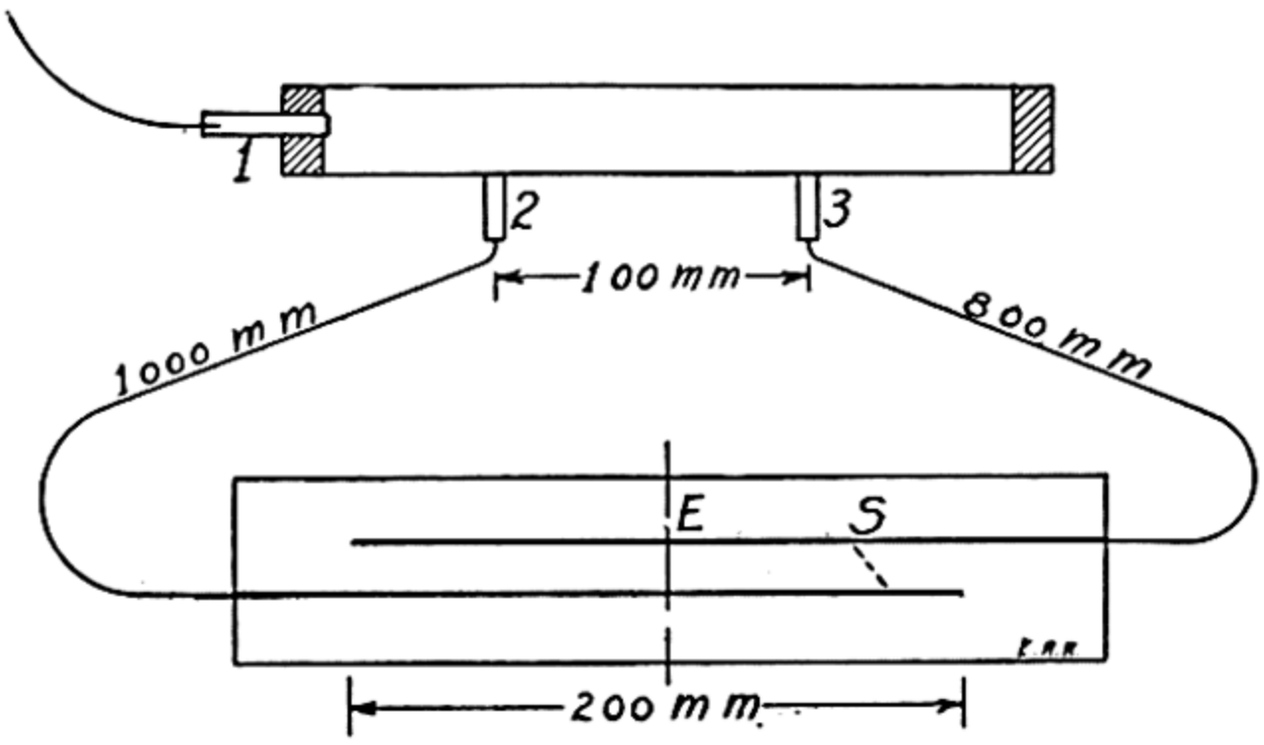


FIGURE 238.—Dautriche test for velocity of detonation; 1, main fuse; 2, and 3, detecting fuses. The distance *E-S* is measured.

booster charge, placed between the detonator and the bursting charge, to assure the detonation of the larger quantity of less-sensitive high explosive.

Commercial explosives such as the dynamites require a blasting cap for detonation and a fuse [2] or electric spark to set off the cap. Sometimes a lead tube filled with TNT or PETN (called a cordeau) is used as a booster. These items are fastened on or inserted after the main charge is in place. A round of ammunition is composed of several different explosives assembled so that each serves a definite function [3] (see Figure 239).

Some Principles of Explosives Technology [4]

Most chemical explosives contain oxygen and oxidizable elements. The oxygen is usually present in groups having low thermodynamic stability (labile radicals) such as the nitrate ($-ONO_2$), nitro ($-NO_2$), or nitramine ($-NH \cdot NO_2$) groups. Other "explosophore" groups are the chlorate

[2] The Bickford fuse has a core of black powder in a tube of woven threads, the outside layer being of waterproof material. It burns at the rate of about one foot per minute; a spit of flame shoots out at the blasting-cap end.

[3] The design of ammunition is an interesting subject. A description of the functions and requirements for cartridge primer and fuse primer (which are frequently different formulations), for propellant igniter and bursting charge detonator, etc., is available in a War Department publication, TM 4-205, "Coast Artillery Ammunition." This pamphlet also provides a description of mechanical base and nose fuses of various types and explains how they work.

Strictly speaking, a "round of ammunition" includes "everything necessary to fire the gun once."

[4] In part adapted from Bebie, *op. cit.*, pages 5-7.

TABLE 127.—*Characteristics and Uses of Explosives.*

Name	Composition or Chemical Formula	Detonation Velocity, Meters/Sec. (a)	Volume of Expansion cc./10g. (b)	Sensitivity to Shock	Major Characteristics	Important Uses
			High Explosives			
Nitroglycerine (N. G.)	$C_3H_5(ONO_2)_3$	7450	515	Very High	Oily liquid, volatile above 50° C.; plasticizes nitrocotton, causes gelation or colloidizing.	Shooting oil wells; a component of dynamites, permissible explosives, double-base powders.
The Dynamites: Straight Dynamites	15 to 60% N. G. in wood meal, with $NaNO_3$ and antacid	Varies with N. G. content		Moderately Low	Cheesy, plastic substance; packed in paper cartridge, may be tamped in hole for greater blasting effect. Fired by detonator. Dangerous to thaw after freezing. Sensitive to friction, heat. Water displaces N. G.	Blasting of hard rocks, stumps, coal and other minerals. Demolition.
Ammonia Dynamites	As above, except NH_4NO_3 replaces part of N. G.	9,100-13,000 Varies with N. G. content		Low	Cheaper than straight dynamites for equal strength.	Blasting soft rock, hard earth; permissible for coal mining (some grades).
Low-Freezing Dynamites	Similar to straight or ammonia types, but with ethylene glycol dinitrate replacing part of N. G.			Low	Freezing point below 0° C.	All U. S. dynamites are low-freezing type.
Gelatine Dynamite	Mixture N. G. with 2-6% collodion cotton, balance wood or cereal meal, nitrates, etc.	6100 Varies with N. G. content	415	Low	Jelly-like substance. Very powerful. Water-proof.	Used where maximum shattering effect is desired; submarine blasting.
Blasting Gelatine	N. G. plus 7-8% of collodion cotton	7800	520	Moderately Low	Strongest, quickest, most waterproof of commercial explosives.	Tunnel driving, deep well shooting, and submarine work.
TNT, Tri-Nitro-Toluene	$CH_3 \cdot C_6H_2(NO_2)_3$	6800	260	Low	Easily melted for casting into shell or blocks (M. P. 80.3° C.). Black smoke on explosion.	Bursting charge in shells and bombs; blocks used for demolition and for underwater explosions. Used in mixtures to lower casting temperature.
Amatols	(1) 50% TNT, 50% NH_4NO_3 (2) 20% TNT, 80% NH_4NO_3	6900 5100	300 Under 300	Low Low	(1) Easily cast into shells, (M. P. about 85° C.). (2) Shell filled by pressing. Both give white smoke, strength equal to TNT.	(1) Bursting charges in shell. (2) Used in large caliber shell. Considered as a substitute for TNT by U. S. armed forces.
Ammonium Nitrate Mixed Explosives	60% NH_4NO_3, 15% TNT, 18% aluminum, 7% charcoal (example)	Variable to suit use. Control particle size.		Low	Sometimes defective in propagation.	One of the most popular types of permissible explosives.
DNT, Di-Nitro-Toluene	$CH_3 \cdot C_6H_3(NO_2)_2$			Low	Reduces velocity of explosion and density when mixed with other explosives.	Used in mixtures; up to 20% with TNT in bursting charges; about 5% in FNH (flashless) propellants; 6% in small-arms ammunition (with guncotton).

TABLE 127.—*Characteristics and Uses of Explosives (Continued).*

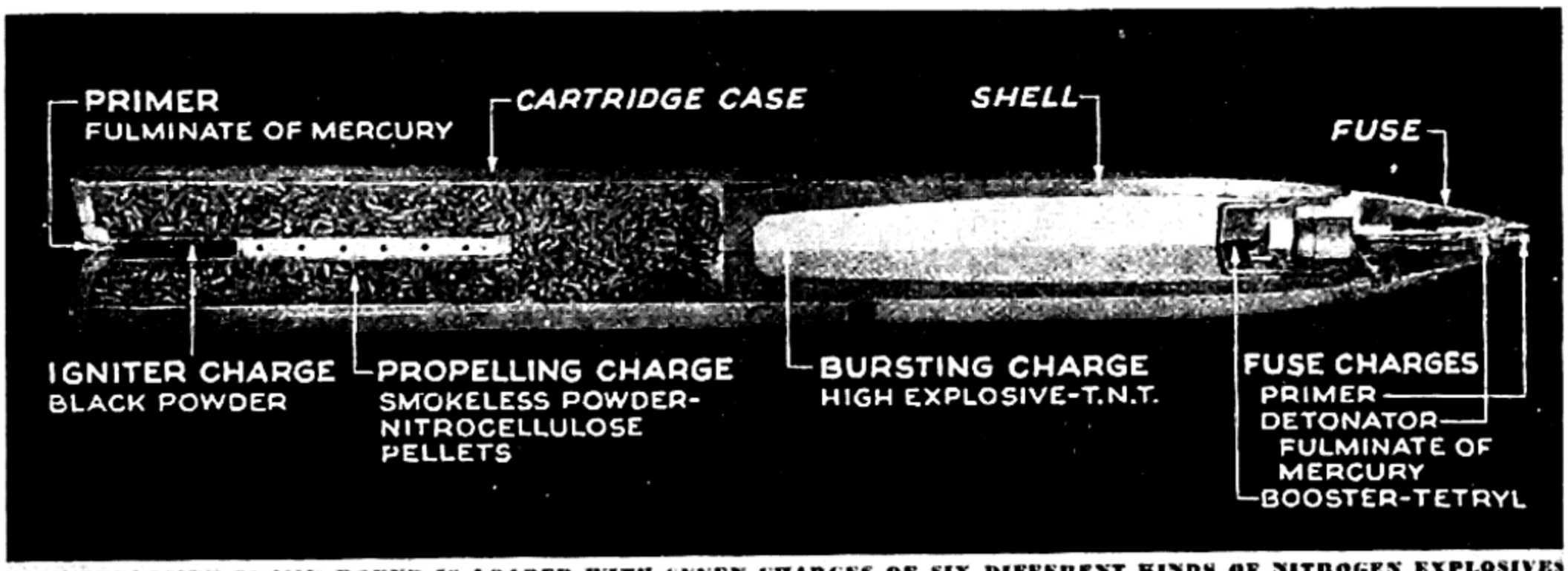
Name	Composition or Chemical Formula	Detonation Velocity, Meters/Sec. (*a*)	Volume of Expansion cc./10g. (*b*)	Sensitivity to Shock	Major Characteristics	Important Uses
RDX, Cyclonite.	Sym. Trimethylene-Trinitramine	8400		Moderately High	Decomposes on melting at 200° C. Must be used in a desensitized mixture. 50% more powerful than TNT.	Bursting charge in shells and bombs. Mixed with wax for press-loading; slurried with TNT for casting.
Torpex	Mixture of RDX, TNT, and aluminum powder			Low	Very powerful.	Under-water explosive; used in anti-submarine munitions.
Hexonit	Mixture of N. G. and PETN, with at least 10% RDX				One of the most powerful high explosives.	
Haleite (EDNA)	Ethylene dinitramine, $O_2N \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot NO_2$			Less Than RDX	More powerful than TNT, less than RDX.	Similar to RDX.
Picric Acid 2,4,6-Trinitro-Phenol	$(OH)C_6H_2(NO_2)_3$	7000	300	Moderately High	Hazardous to cast (M. P. 120-123° C.); unstable in summer heat; forms dangerous metallic picrates with copper, etc.	Limited to some boosters and as a partial substitute for mercury fulminate; may be used with other explosives which lower M. P. (bursting charge).
Ammonium Picrate (Explosive D)	$(ONH_4)C_6H_2(NO_2)_3$	6500	230	Very Low	Insensitive to shock and friction. Melts with decomposition; shells must be filled by tamping or pressing. Less power than TNT.	Armor-piercing shell.
Nitrostarch	Mixture of various nitric esters of starch			Low	Highly inflammable white powder.	Ingredient of blasting explosives; demolition.
Tetryl; Trinitro-Phenyl-Methyl-Nitramine	$(NO_2)_3C_6H_2 \cdot N \cdot CH_2NO_2$	7200	340	Moderately High	Too sensitive for general use as a bursting charge; less sensitive when compressed in small quantities.	Booster charge in H. E. shells to detonate bursting charge; with fulminate primer in blasting caps. Bursting charge in anti-aircraft shells (40 mm.).
PETN; Penta-Erythritol Tetra-Nitrate.	$C(CH_2ONO_2)_4$	8000		High	One of the most powerful high explosives.	Booster charge similar to tetryl; in detonating tubes (Cordeaux). Demolition.
Pentritol	Mixture, approx. equal parts TNT and PETN.			Low	Very powerful.	Bursting charge.
				Initiators		
Mercury Fulminate	$Hg(ONC)_2 \cdot \frac{1}{2}H_2O$	3920	213	Very High	Easily detonated by impact of firing pin or spark; usually mixed with others to reduce sensitivity or to produce flame.	Commercial blasting caps; fuzes for shells; propellant primers; small-arms cartridge caps.
Lead Azide	$Pb(N_3)_2$	5000	250	High; (⅓ of Fulminate)	Requires higher temperature for detonation than fulminate; therefore, safer to handle.	Primers and impact fuzes. With silver acetylide in blind rivets.
Lead Styphnate, Lead Trinitro-Resorcinate.	$C_6H(NO_2)_3(O_2Pb)$			High	More easily ignited than lead azide.	Alone or with lead azide in primers, etc.

				Propellants		
Colloidal Nitro-Cellulose (N. C.) Powders.	Pyrocotton: cellulose nitrate with 12.6% N	Variable with surface area		Low	Burning rate controlled by graining; hygroscopic; smokeless flame, with intense flash. Gelatinized with alcohol-ether.	Combined with stabilizers and modifiers to make smokeless powders for artillery, small-arms and sporting ammunition.
	Guncotton: cellulose nitrate with 13.2% N				Pyrocotton and guncotton are usually blended to secure an average of 13.15% N.	Dry guncotton in fiber form is used in primers fired by an electric current.
Double-Base Powders	60 to 80% nitrocellulose 40 to 20% nitroglycerine			Low	Very rapid burning rate; controllable by surface area. More powerful and more readily ignitable than straight N. C. powders. Causes erosion of gun bores.	Propellant for mortars and sporting ammunition; not used by U. S. armed forces as cannon powder because of bore erosion.
Cordite	65% N. C., 30% N. G., 5 vaseline			Low	Gelatinized with acetone.	Propellant for large caliber naval guns (English).
FNH (Flashless Non-Hygroscopic) Powders	Either straight N. C. or double-base powders with additions of coolants, etc., to prevent muzzle flash, and decrease water absorption.			Low	Like other smokeless powders, but can be rolled into sheets. Heat of explosion absorbed by DNT, potassium salts, etc.	Propellant for small armor-piercing rockets such as the "Bazooka" (N. G. base); for naval ammunition (N. C. base).
Albanite; DINA Powder	Di-(2-nitro-oxyethyl)-nitramine.			Low	Better flashless powder than FNH powders.	Naval ammunition.
Rocket Powder (Solventless Powder).	Nitrocellulose plasticized with about 50% N. G., plus stabilizers and potassium salts.			Low	Very rapid, uniform burning rate; can be made with thick section since no solvent need be removed.	For rockets up to 4.5 inch.
Chemical Propellants.	Hydrogen peroxide, 80-90% H_2O_2, plus Ca, Na, or K permanganate (solid or aqueous solution).				Catalytic decomposition into water and O_2 releases about 1000 btu. per pound. Supplies oxygen to burn petroleum fuel.	For driving turbines on submarines, V-2 rocket fuel pumps; jet motors; launching device for ram-jets.
	Hydrazine hydrate plus methyl alcohol.				Rapid combustion; fuel and oxidizer are both liquid.	For torpedo turbine drives.
	Fuming nitric acid—aniline				Rapid rate of reaction. Generates heat and gases.	For launching device for ram jets; jet motors.
	Mixed acid—monoethylaniline				As above.	As above.
				Miscellaneous		
Black Powder	75% KNO_3 (or $NaNO_3$), 15% charcoal, 10% sulfur. (Example.)	400	50	Low	Cheap; not shattering; persistent smoky flame.	Blasting cartridges (coal mining); time (delay) fuses for blasting and shell; in igniter and primer assemblies for propellants. Pyrotechnics. $NaNO_3$ powder for practice bombs and saluting charges.

(a) Velocity of detonation may be measured by the Dautriche test. Approx. value; varies with density.

(b) Normal Trauzl block test: 10 grams of explosive are placed in a cast lead cylinder 200 mm. x 200 mm. which has a 25 mm. dia. hole 125 mm. deep. The explosive is wrapped in tinfoil. A No. 8 cap containing 2 gm. mercury fulminate is inserted and the remaining cavity packed with sand. The values above are the increase in volume of the bore after explosion.

($-ClO_3$), perchlorate ($-ClO_4$), and the fulminate ($-ONC$), which contain oxygen, and the azide ($-N=N\equiv N$) and acetylide ($-C=C-$) groups, which contain no oxygen. Inorganic nitrates and perchlorates are used in combination with sulfur and charcoal, or other easily oxidized materials. Organic compounds such as cellulose nitrate or trinitrotoluene have the oxygen and combustibles in the same molecule. Some organics, like nitroglycerin, have more than enough oxygen for complete combustion. Others such as TNT are deficient in oxygen, and a black smoke accompanies explosion. The addition of ammonium nitrate, which has an excess of oxygen, will correct this negative oxygen balance.



HIGH-EXPLOSIVE 75-MM. ROUND IS LOADED WITH SEVEN CHARGES OF SIX DIFFERENT KINDS OF NITROGEN EXPLOSIVES

FIGURE 239.—High-explosive 75-millimeter shell is loaded with seven charges of six different kinds of nitrogen explosives, all shown in this picture. (Reproduced from *Life* for March 23, 1942, page 73.)

The principal components of explosion gases are nitrogen, CO, CO_2 and water. The heat of explosion, maximum temperature, volume of gaseous products, and pressure developed in a closed chamber provide a measure of the total energy, but the rate of energy release determines the effectiveness of the explosion. The rate of detonation of a high explosive generally increases with density; casting a molten material into a shell is therefore preferable to loading loose grains and tamping. It is for this reason that the melting point of the explosive is of such practical importance. TNT, with a melting point of 80.3° C., is easily cast, but the casting of picric acid (m.p. 123° C.) is hazardous. It is common practice to make a slurry of a high-melting explosive in TNT, or in some cases to make a eutectic solution of two explosives, to facilitate casting. On the other hand, the burning rate of black powder decreases with increased density; this is the basis for time-delay pellets used in fuses. The rate of burning of a propellant may be controlled by designing the grain so that surface area available for burning increases as the weight of the grain decreases (progressive burning), as in nitrocellulose smokeless powders, which are fluted on the outside and provided with one or more longitudinal perforations. In the case of spherical powders, where the surface decreases with decreasing weight (regressive burning), the surface is coated with a chemical called a deterrent. This decreases the rate of burning while it is present, to match the slower rate prevailing when the diameter of the sphere is less. Heat-absorbing

compounds such as mineral salts, powdered metals, dinitrotoluene, etc., may be added to smokeless powders to make them flashless. Similarly, heat absorbers may be added to blasting powders to control the duration of flame, to make them safe for use under certain mine conditions.[5] A graphite coating applied to grained propellants not only acts as a deterrent, but decreases the hazard of handling by removing static charges, acts as a lubricant to facilitate tamping to a higher density, and increases the ignitability of the powder.

The availability of raw materials frequently governs the choice of explosives in wartime. For example, in the recent war the Italian forces used PETN rather than tetryl as a booster, because the former is made from synthetic methanol, but the latter requires benzene, a coal-tar product; Italy had only a small coal-tar industry. Similarly, the Germans partly substituted diethylene glycol dinitrate for nitroglycerin, when their supply of fats decreased.

Many other factors are considered in evaluating an explosive: the degree of toxicity of the raw materials or intermediates that must be handled in making it; the toxicity or obnoxiousness of the gases produced on explosion; its hygroscopicity or water-repellance, stability in storage, cost of manufacture, and others.

The explosives used for peacetime purposes (industrial explosives) are chiefly the dynamites, black powder, and the ammonium nitrate mixtures (permissibles). PETN and block TNT are sometimes used for demolition of buildings and structures. The mining industries consume about 60 per cent of the industrial explosives produced; railway and other construction, 20 per cent. Coal mining requires practically all the black powder and permissible explosives.

High Explosives

Nitroglycerin (glyceryl trinitrate) is a pale-yellow, oily liquid (colorless when pure) which freezes at 13° C., and is very sensitive to shock. It is made commercially in a steel nitrator which has steel cooling coils and a mechanical agitator. A very pure glycerin [6] is used. About 6800 lbs of mixed acid having the composition 50 per cent HNO_3 and 52 per cent H_2SO_4 (oleum) [7] is charged into the nitrator with agitation and is cooled by the circulation of $CaCl_2$ brine at −20° C. through the coils. A total of about 1300 lbs of glycerin is then added slowly in a steady stream. The tem-

[5] For use in gaseous or dusty mines, explosives must pass tests conducted by the U. S. Bureau of Mines. If approved, they are placed on a "permissible list." Permissibles are usually ammonium nitrate explosives, compounded to suit specific conditions. For a list of available U. S. brands, see Bebie, *op. cit.*, page 118.

[6] 99.9 per cent purity. See also Chapter 32.

[7] A mixture of nitric and sulfuric acid is commonly used for organic nitration reactions because the sulfuric acid is capable of forming a hydrated molecule thereby effectively removing one of the products of any nitration reaction, i.e., water. This shifts the equilibrium to the right, allowing more of the nitrated product to form, resulting in a higher yield than would otherwise be possible. The sulfuric acid does not otherwise take part in the reaction and normally is completely recovered for re-use, except for minor wastage.

perature of nitration is 2 to 3° C.,[8] if there is any tendency for the temperature to rise, the flow of glycerin is stopped. The addition step takes about 50 to 60 minutes; agitation is continued a few minutes and then the spent acid is allowed to separate from the oily nitrated glycerin. The spent acid carries away in solution about 5 per cent of the total yield. The acid is given an additional settling, then is denitrated for recovery of the HNO_3 and H_2SO_4. The glycerin trinitrate is washed with warm water, then with a 2 to 3 per cent Na_2CO_3 solution, and finally with a concentrated solution of NaCl, which breaks down any emulsion and partly dehydrates the nitroglycerin. The stored product contains about 0.5 per cent water; the storage tanks are lead-lined.

The Dynamites. The high sensitivity of nitroglycerin to shock was a deterrent to its use until the chance discovery by Nobel in 1862 that large quantities of the liquid explosive could be absorbed in kieselguhr (infusorial earth), forming a plastic, cheesy substance which could then be transported and used with relative safety. This original formulation (guhr dynamite) is rarely used now, however, since the presence of 25 per cent of inert kieselguhr diminishes the blasting effect by absorbing energy. The absorbent used today is generally wood meal (pulp, flour, or sawdust), or cereal meal, to which is added an oxidizer such as sodium nitrate and a small amount of antacid ($CaCO_3$, ZnO). Various amounts of nitroglycerin may be used in the formula, depending on the strength desired. The commercial *straight dynamites* contain from 15 to 60 per cent.[9] Ethylene glycol dinitrate ($O_2NO \cdot CH_2 \cdot CH_2 \cdot ONO_2$) or other explosive oils[10] are now added to all domestic dynamites to make them *low-freezing*. Nitroglycerin may be gelatinized with 7 to 8 per cent of collodion cotton to make *blasting gelatin*. *Gelatin dynamite* corresponds to a mixture of 45 to 65 per cent blasting gelatin with 55 to 35 per cent of mixed dope (wood pulp plus nitrates).

Straight dynamites have been replaced for many uses by the *ammonia dynamites*, which provide the same blasting strength but contain only two-fifths as much nitroglycerin. They are therefore much cheaper, but they have not quite the brisance[11] and cannot be used for blasting hard rock, where a shattering effect is desired. These are really ammonium nitrate explosives in which the nitroglycerin is used to sensitize the NH_4NO_3 to detonation. *Ammonia gelatin dynamites* have a greater shattering effect;

[8] This is below the freezing point of nitroglycerin, but in acid solutions the oil will not freeze to the coils if there is sufficient agitation. Adapted from "Explosives Manual," Lefax, Inc., Philadelphia, Chap. XI, part 2.

[9] "A 40% straight dynamite" contains 40% N.G., 44% $NaNO_3$, 14% carbonaceous material, 1% antacid, 1% moisture. A "40% ammonia dynamite," with the same strength, contains 15% N.G., 32% NH_4NO_3, 38% $NaNO_3$, 4% sulfur, 9% carbonaceous material, 1% anacid, 1% moisture.

[10] Dinitromonochlorhydrin and tetranitrodiglycerin are also used.

[11] A test for comparing the brisance of explosives is the sand bomb test: 80 grams of standard Ottawa sand, sized to minus 20 plus 30 mesh, is placed in a thick-walled cylinder. A cap containing 0.400 gms. of the explosive is then inserted and the remainder of the cavity filled with 120 gms. of sand. The explosive is suitably detonated. The weight of sand which then passes 30 mesh screen is a measure of the brisance of the explosive. For further details see "Laboratory Manual of Explosive Chemistry," Olsen and Greene. New York, John Wiley and Sons, page 80 (1943).

cent charcoal, and 10 per cent sulfur. A slow-burning powder contains 59 per cent KNO_3, and by blending the two types, powders suitable for time fuses are obtained. For blasting, a weaker powder may be used: 40 per cent nitrate, 30 per cent charcoal and 15 per cent sulfur. Its manufacture is a series of batch operations. The finely ground components are moistened and kneaded together in a sigma-blade mixer, then milled in an edge-runner to make a more homogeneous mixture. The mass is pressed into dense cakes which are then granulated and dried; this is followed by screening to various sizes; the dust is used in pyrotechnics and to make fuses, and the oversize is recrushed. The sized grains are "polished" and provided with a coating of graphite by tumbling in rotating cylinders or coating pans. The blasting cartridge (coal-mining) is a single cylindrical piece with one perforation in the long axis, formed by extruding a paste made of the proper sized grains. All the operations from granulation to screening are dangerous, and are performed by remote control, the machinery being in barricaded buildings.

Propellants

Since the late 1860's the universal propellant for projectiles has been smokeless powder, the main ingredient of which is colloidal nitrocellulose. Double-base powders include nitroglycerin in the formulation; the powder then has a greater heating effect and is more powerful; a smaller charge produces the same muzzle velocity. Single- and double-base powders may be used as perforated grains or as spherical (ball) powders. The plasticizing effect of nitroglycerin allows double-base powders to be used in tubes, sheets, flakes, discs, and thick-webbed rocket propellants.

Nitrocellulose Manufacture: The result of treating cellulose fibers with nitric acid is a complex ester in which all or most of the hydroxyl groups in the fundamental cellulose unit [20] have been replaced by nitrate ($-ONO_2$) groups. The reaction proceeds according to the equation:

$$\underset{\textit{Sugar unit in cellulose}}{C_6H_7O_2(OH)_3} + 3HNO_3 \leftrightarrows \underset{\textit{cellulose trinitrate}}{C_6H_7O_2(ONO_2)_3} + 3H_2O$$

In practice, the trinitrate (14.16 per cent N_2 content) is not formed, but nitration is stopped when the nitrogen content has reached a lower value. *Pyroxylin* (collodion cotton) contains 10.8 to 11.6 per cent N_2; it may be plasticized with camphor in the presence of alcohol under heat and pressure to make Celluloid. By carrying the nitration to the level of 12.6 per cent N_2 (plus or minus 0.1 per cent), the low explosive called *pyrocotton* is produced. The highest nitration level is represented by *guncotton*, which contains 13.2 per cent N_2 or slightly more.

The manufacture of nitrocellulose generally starts with cotton linters [21] which have been purified of pectic matter, wax, and minerals by boiling with caustic soda solution and bleaching with calcium hypochlorite solution.

[20] There is some disagreement as to how small the fundamental unit is; actually, molecular weights up to 300,000 have been observed for the cellulose molecule.

[21] The short cotton fibers not suitable for textiles. Specially purified sulfite pulp waste cotton and paper may be used for some purposes.

After drying, the linters are fluffed, weighed (30 to 32 lbs per batch) and charged into a steel nitrator into which about 1500 lbs of mixed acid [22] has previously been charged. The mass is agitated over a period of 25 to 30 minutes; the temperature is 20 to 30° C. Nitrogen oxide fumes are evolved and vented. The balance of the operations may be summarized as follows: [23]

Centrifuging: to remove most of the spent acid (which may be denitrated or fortified as in TNT manufacture).

Washing: by boiling with dilute Na_2CO_3 solution, then treating with successive washes of alternately hot and cold water, and finally boiling for about 70 hours. It is then transferred to beaters (Chapter 21) to break up the fibers and to complete the washing operation.

Poaching: a repetition of the washing steps (using dilute soda ash and then boiling with several changes of water). This is necessary after the fibers have been passed through the beaters to assure removal of the last traces of acid.

Testing for stability and nitrogen content; final centrifuging, and storage.

Perforated-Grain Powders: Fibrous nitrocellulose has too high a burning rate to be used as a propellant; it must be colloided to decrease its surface, then shaped into a usable form. To make perforated grain powders, the fibrous material is compacted in a hydraulic press and ethyl alcohol is percolated through the mass. Water is displaced by the alcohol, and the pressure is such that a definite percentage of alcohol is retained. The block from the press is then shredded and mixed with ether [24] in a water-jacketed machine. Whereas the nitrocellulose is insoluble in alcohol or ether alone, it is gelatinized by the resulting mixture (about 1 part alcohol, 2 parts ether), losing its fibrous form and becoming a brown, clear, jelly-like mass. This is compressed and extruded into long, thin strands by a "macaroni" press, which operation serves to improve the homogeneity of the material. The macaroni is charged to another hydraulic press and extruded through dies which not only provide a scalloped outer surface, but form one or more perforations in the cords, which are then machine-cut to definite lengths to form grains. Most of the solvent is removed by drying, the remaining solvent being extracted by a lengthy water wash, after which the grains are placed in warm-air driers for a period of 48 to 72 hours. For most purposes, pyrocotton and guncotton grains are blended in a wooden tower (with inclined baffles) to produce a powder having an average nitrogen content of 13.15 per cent.

The Ball-Powder Process.[25] For small arms ammunition and up to 37-mm cannon shell, a spherical powder has been developed. It is made by a radically different process which converts cellulose nitrate into propellant

[22] Its composition averages 21 per cent HNO_3, 63 per cent H_2SO_4, 1 per cent nitrosyl sulfuric acid, and 15 per cent water.

[23] For a pictured flow sheet see *Chem. Met. Eng.*, 49, No. 4, p. 76 (1942). Compare also related matter in Chapter 31, this volume.

[24] Diphenylamine is added at this point, as is nitroglycerin, if double-base powder is being made. The function of the amine (stabilizer) is to react with any trace of nitrous, nitric or sulfuric acid that may be released due to decomposition of the powder in storage; such traces catalyze further decomposition, if not neutralized.

[25] "Ball Powder Process Upsets Explosives Industry Tradition," T. R. Olive, *Chem. Eng.*, 53, No. 12, 92 (1946).

powder in one-fifth the time required to make perforated grain powders. Starting with the fibrous nitrated cotton (13 per cent N_2 for this process) after the first boiling operation, the lengthy cold and hot washings, the beater and the poaching steps are eliminated; the cotton is used as it comes from the second centrifuge. Colloiding is performed in one tank, and proceeds as follows: A charge of 7000 lbs of nitrocellulose is dissolved completely in ethyl acetate. A stabilizer (diphenylamine) is added, and also nitroglycerin, if a double-base powder is to be made. Chalk is used to neutralize any residual nitrating acid. The speed of the agitators is now changed to produce a shearing effect, and a glue-like colloid is added to cause the acetate-nitrocellulose lacquer to break down into droplets, which gradually assume a truly spherical shape ("ball formation"). Water is removed from the spheres by the osmotic pressure gradient that exists when a salt such as sodium sulfate is added to the water phase of the emulsion. The batch is then brought to a boil to remove the ethyl acetate solvent; the ball powder is screened and washed, given a surface coating of a deterrent (dibutyl phthalate), dewatered on a top-feed rotary filter, and dried in a conveyor-type infrared drier. Finally, the balls are glazed with graphite, screened to size,[26] and blended for uniformity.

Rocket Propellants

The military definition of the term "rocket" is: a self-propelled projectile carrying a fuel of sufficient oxygen content to require no outside air for its combustion.[27] Double-base powders are admirably suited for such a fuel. The anti-tank weapon, or "bazooka," fired a rocket in which the propellant was solvent-type powder extruded into grains somewhat longer

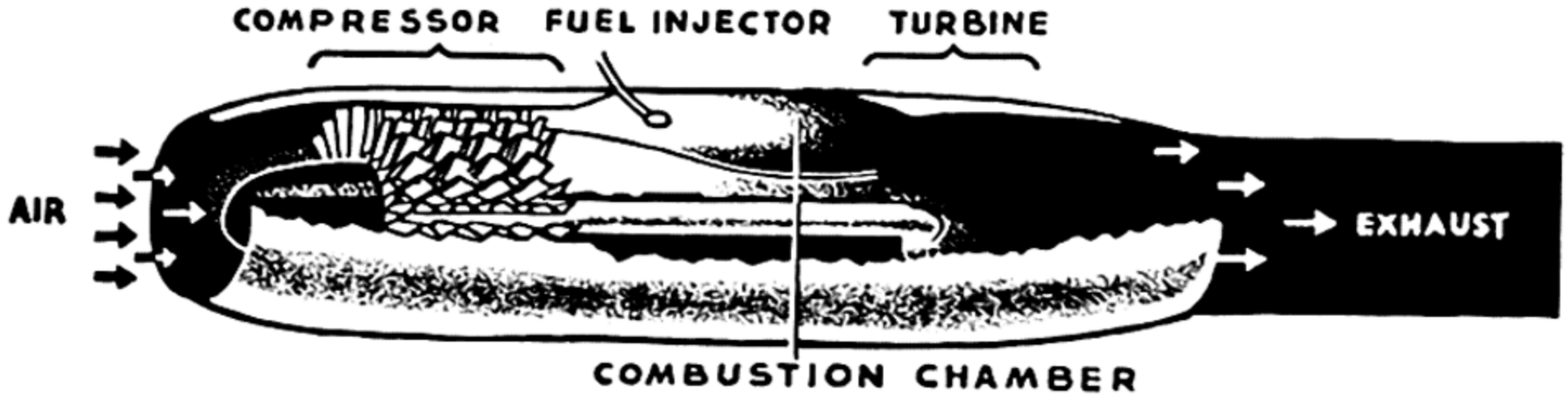


FIGURE 240.—In the turbojet engine (above) for driving an airplane, air enters the front of the engine, is compressed, and meets gasoline or kerosine which burn in it at rapid rates. The expanding gases activate a turbine which operates the compressor, and then pass out the nozzle at the rear, driving the plane forward. (From the *New York Sunday Times*.)

than those used in cannon powder. The propellant was completely burned before the projectile left the light-weight launcher tube, not only to protect the operator from flame, but to assure flight stability and accuracy. At the

[26] From 0.006 to 0.030" diameter. The size is controlled within narrow limits in the ball-forming step by temperature, lacquer viscosity (percentage solvent), agitation time, agitator speed, and type of colloid added.

[27] For a discussion of rocket powders and their manufacture, see *Chemical Industries*, **57**, No. 1, 65 (July 1945), and **57**, No. 4, 634 (Oct. 1945).

same time, the combustion rate was slow and uniform enough, because of the design of the grain, so that only thin-walled tubing was required to withstand the pressure. Propulsion was by a jet reaction. To make the larger rockets (up to 4.5″ diameter), such as were fired from shipboard or

FIGURE 241.—The ramjet shown above is the simplest of jets; it is dubbed the "flying stovepipe." It must be launched at over 400 mph., at which speed air is rammed into the engine, the fuel is burned and exhausted through the tail, and the jet is driven forward. (From the *New York Sunday Times*.)

aircraft, it was necessary to develop solventless powders, since the powder stick had to be designed to fit snugly into this large cylindrical shell so as not to fall out the opening at the rear, and also to make the best use of the available space and to obtain proper burning characteristics. This required a cruciform shape having relatively thick sections. The powder used by the United States forces is formulated of guncotton plasticized with approxi-

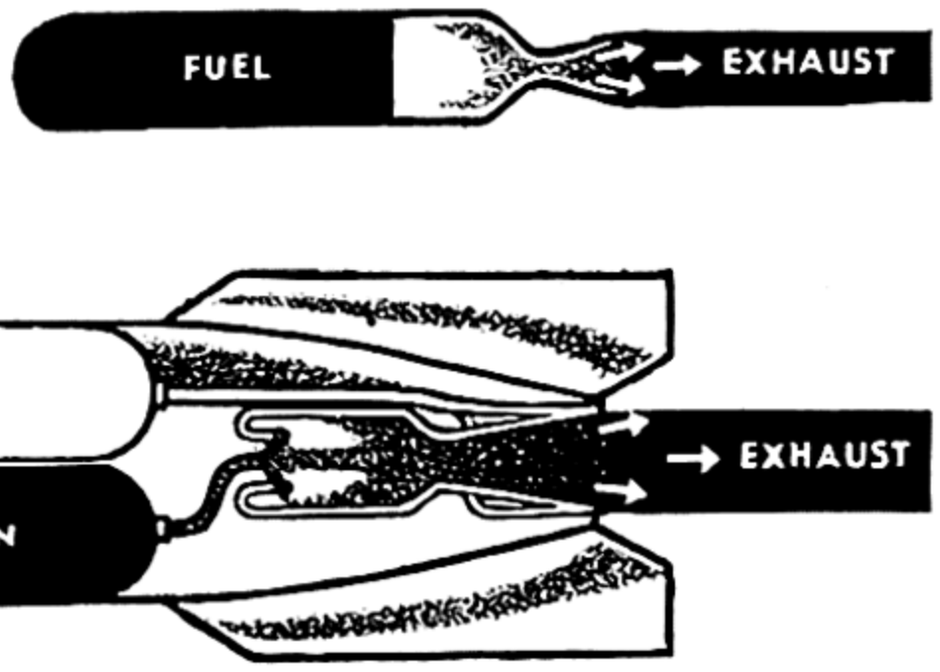


FIGURE 242.—The rocket shown in the lower sketch carries its own oxygen so that it can operate outside the earth's atmosphere. (Explosives in war-head not shown.) The V-2 rockets use liquid fuel which is burned in oxygen from liquid oxygen. The upper sketch shows a short range rocket which uses solid fuel and operates like the fireworks skyrockets. (From the *New York Sunday Times*.)

mately an equal weight of nitrocellulose, plus diphenyl urea (Centralite) which acts as both stabilizer and plasticizer, plus another plasticizer, diphenyl phthalate, and potassium sulfate. The latter helps to control burning rate as well as to reduce the flash.

The solventless rocket sticks are made in the following way: the ingredients of the explosive are blended and passed through a colloid mill, then dewatered by centrifuging, and dried. Several lots are blended and made into a water paste which is then weighed into 6½ lb increments. These small batches are individually masticated on heated "differential rolls" similar to those used in rubber compounding. As the water cooks out, the material becomes colloidized, and sheeted. Several sheets are worked together on

"even-speed rolls," then rolled up to make a cylindrical block charge for the extrusion press, which produces the cruciform shape. The work rooms are heated, and the material is reheated several times to retain its plasticity. Internal fissures in the grain and the presence of foreign materials are detected by an automatic supersonic device, or by x-ray.

Powder-propelled rockets are limited in size. To carry larger "pay loads," combination fuels are used. The German V-2 bomb, carrying 1850 lbs of high explosive at a maximum speed of about 4000 miles per hour, was fueled with 4½ tons of alcohol and 5½ tons of liquid oxygen. All of the fuel was burned within 65 seconds. But consider that all of that fuel was pumped into the combustion chamber in such a short space of time by a small pump which utilized 4000 horsepower.[28] That power was generated by the catalytic decomposition of hydrogen peroxide into oxygen and steam.

The energy released when hydrogen peroxide [29] is decomposed may be used in several ways. In submarine turbines, the peroxide passes over a bed of solid calcium, sodium, or potassium permanganate.[30] The oxygen is used to burn a petroleum fuel, and the water from the peroxide plus the sea-water cooled condensate from the turbine are converted into high temperature steam; it is a self-contained system. As a propellant for the launching device used with ram-jets (the German V-1, for example), a solution of one of the permanganates is mixed with the peroxide and propulsion is obtained by jet reaction from the escape of the hot gases. Some jet aircraft utilize the peroxide-catalyst-fuel combination.

Other "chemical propellants" used for jet propulsion include fuming nitric acid and aniline and its counterpart, mixed acid-monoethylaniline; the heat and rapidity of the chemical reaction generates the necessary hot gases. The reaction between hydrazine hydrate and methyl alcohol has been used to drive submarine torpedoes which have exceptional performance and are essentially wakeless.

Other Patents

1,849,356, an explosive nitrocellulose grain surface treated with tetranitroaniline; 1,775,271, a nitroglycerin cell, container for charge in shooting wells; 1,814,980, manufacture of TNT; 1,868,388, on diethylglycol dinitrate (A. Hough); 1,828,788, improved explosives of the dynamite and gelatin type; 1,820,567-8, explosives consisting of sodium chlorate, sodium nitrate, TNT, ortho-nitrotoluene and sawdust; 1,819,457, process of making a colloidal starch explosive.

U. S. Pat. 2,235,060, low density blasting explosive; 2,069,612, ammonium nitrate blasting explosive; 2,033,196, pulverulent dynamite; Brit. Pat. 494,277, surface treating agents for smokeless powder. U. S. Pat. 2,261,195, explosive charges for detonating rivets; 2,213,255, smokeless powder.

Reading References

"Explosives, their history, manufacture, properties and tests," A. Marshall, Philadelphia, P. Blakiston's Sons & Co., 2d ed., 1932.

[28] As reported by Joseph and Stewart Alsop in the *Saturday Evening Post*, September 6, 1947.

[29] For this purpose the hydrogen peroxide must be concentrated to 80 to 90 per cent H_2O_2. See Chapter 18 for its manufacture. The heat of dissociation of 80 per cent peroxide is about 1000 Btu per lb.

[30] See *Mechanical Engineering* for December 1946, page 1045; also *Ind. Eng. Chem.*, 38, p. 160 (Feb. 1946).

"The manufacture of ammonium nitrate," E. M. Symmes, *Chem. Met. Eng.*, 26, 1069 (1922).

"The modern high explosives," Manuel Eissler, New York, John Wiley and Sons, Inc., 1924.

"Chimica delle Sostanze Explosive," Michele Giua, Milan, Ulricho Hoeple, 1919.

"The relation of cotton to explosives," R. G. Woodbridge, *J. Chem. Ed.*, 7 (2), 1832 (1930).

"Physical testing of explosives," C. E. Munroe and J. E. Tiffany, *Bur. Mines Bull.* No. 346 (1931).

"Production of Explosives," *Bur. Mines. Tech. Paper,* No. 478.

"Our chemical industry in war time," C. R. Robinson, *Chem. Met. Eng.*, 46, 754 (1939).

"Elements of ordnance," Colonel Thomas J. Hayes, New York, John Wiley and Sons, 1938.

"Military explosives," a technical manual issued by the War Department, TM 9-2900, August 29, 1940. Government Printing Office, Washington, D. C.

"Ordnance safety manual," by the Office of Chief of Ordnance, December 1, 1941, O. O. Form 7224. Government Printing Office, Washington, D. C.

"Coast artillery ammunition," a technical manual issued by the War Department, February 17, 1940. Government Printing Office, Washington, D. C.

"Making explosives for World War II," Jules Bebie, *Chem. Met. Eng.*, 48, 76 (1941).

"The chemist and chemical engineer in the explosive industry," David E. Pearsall, *J. Chem. Ed.*, 16, 121-128 (1939).

"Industrial and military explosives," R. W. Cairns, *J. Chem. Ed.*, 19, 109 (1942).

"Condensed Chemical Dictionary," 3rd ed., section on explosives, pp. 287-292, New York, Reinhold Publishing Corp., 1942.

"Laboratory manual of explosive chemistry," Allen L. Olsen and John W. Greene, New York, John Wiley and Sons, 1943.

"Chemistry, Science in World War II," edited by W. A. Noyes, Jr., Boston, Little, Brown & Co., 1948.

"Direct determination of burning rates of propellant powders," B. L. Crawford, Jr., Clayton Huggett, Farington Daniels and R. E. Wilfong, *Ind. Eng. Chem.*, (*Anal. Ed.*) 19, 630 (1947).

"Dinitromethylaniline as an intermediate in the manufacture of Tetryl," A. Garrett Hill and Kenneth H. Klipstein, *Tr. Am. Inst. Chem. Eng.*, 42, 527 (1946).

"The manufacture of R.D.X. in Great Britain," Part I, W. H. Simmons, A. Forster, R. C. Bowden, *Ind. Chemist (London)*, 24, 429 (1948); Part II, "Raw materials and ancillary processes," p. 530.

"Modern Propellants employed in British ordnance," J. N. Spring, *Ind. Chemist,* 24, 467 (1948).

"A critical review of German long-range rocket development," W. G. A. Perring, *J. Am. Rocket Soc.* p. 1-18 (March, 1946).

"Research and development at the jet propulsion laboratory, Galcit," The California Institute of Technology, *J. Am. Rocket Soc.*, June and September 1946, p. 2-22.

"The rating of rocket fuels," rocket fuels using atomic energy as a primary heat source, Thomas S. Gardner, *J. Am. Rocket Soc.*, June and September 1946, p. 23-26.

"Liquid propellant rocket development," M. W. Nesbitt, *J. Am. Rocket Soc.*, p. 1-11 December, 1946.

"Going up for keeps," Martin Mann, *Popular Science Monthly,* March 1947, p. 66-75, contains a good description of the V-2 rocket.

"Hydrogen peroxide for propulsive power," Capt. Logan McKee, U. S. N., *Mechanical Engineering,* 1045-8 (December, 1946).

"Chemical propellants, the system hydrogen peroxide-permanganate," F. Bellinger, H. B. Friedman, W. H. Bauer, J. W. Eastes, J. H. Ladd, J. E. Ross, Chem. Warfare Service, Edgewood Arsenal, Md., *Ind. Eng. Chem.*, 38, 160 (1946). "Chemical propellants, corrosion and stability studies," F. Bellinger, H. B. Friedman, W. H. Bauer, J. W. Eastes, and W. C. Bull, Chem. Warf. Serv., Edgewood Arsenal, Md., *Ind. Eng. Chem.*, 38, 310 (1946).

In the latter part of the period between World Wars I and II, the application to warfare of all the scientific disciplines increased rapidly in importance. World War II accelerated the pace. Chemical warfare shifted in emphasis from poison gas to incendiaries, outstanding advances being made in the utilization of petroleum for this purpose.

Chapter 34*

Chemical Factors Other Than Explosives in Warfare

The use of chlorine gas against an unprotected enemy by the German Army at Ypres on April 22, 1915, marked a new era in modern warfare. The popular opinion is that this form of warfare was original with the Germans; such, however, is not the case. In milder form, chemicals have been used in warfare for many centuries. The first recorded effort to overcome an enemy by the generation of poisonous and suffocating gases seems to have been in the wars of the Athenians and Spartans (431-404 B.C.) when the latter besieged the cities of Platea and Belium. The attackers saturated wood with pitch and sulfur and burned it under the walls of these cities in the hope of choking the defenders and rendering the assault less difficult. Similar use of choking and poisonous gases is recorded in the history of the Middle Ages, and more recently during the siege of Charleston, S. C., during the Civil War.

Modern chemical warfare embraces the field of toxic chemicals, screening smokes and incendiaries, with methods of dispersal or projection of such agents, and means of protection against them. In chemical warfare parlance, the word "gas" is used in a broad sense, and denotes any substance, solid, liquid or gaseous, which is dispersed in the air and which irritates the lungs, eyes or skin of the enemy's forces. Poison gas warfare, it is true, was outlawed on a moral basis by a pact between the major nations signed at the Geneva Convention [1] in 1925; nevertheless, it is mere caution to assume that the belligerent in any world conflict might use gas, when hard pressed,[2] and that a high level of preparedness against it is justified. The fear of retaliation is undoubtedly the greatest single deterrent to its use; in addition, the mobile nature of ground warfare has made the use of poison gas unattractive from a purely military standpoint.

During World War II, gas was not used on a major scale. The fine work by scientists in and out of the Government service was directed mainly to improvements in methods of manufacture. In other directions, major advances of immediate utility were recorded. The effectiveness of aerial incendiary raids in crippling enemy industrial establishments and their effect upon the morale of the population of cities was early recognized, and new types of bomb fillings, such as "goop," resulted from wartime research. The

* In collaboration with A. Robert Fowler, Chemical Engineer, Niagara Falls, N. Y.

[1] The United States and Japan were two nations that did not sign the Convention pact.

[2] "Chemical Warfare and the Chemical Warfare Service" published by the Chemical Warfare Service, U. S. War Department, 1942, page 4.

development of what has been called "petroleum warfare," in which thickened gasoline is used not only as a bomb filling, but as a fiery lance projected by flame throwers, proved to be of considerable importance.

War Gases

The various chemical agents in this category may be solids, liquids, or gases; they are employed either to produce casualties or for their harassing effect. Generally, these agents are classified according to their physiological effect into four groups, as follows:

(1) *Vesicants:* skin-blistering agents, against which a gas mask is insufficient protection.

(2) *Lung irritants:* those which produce burns or intense irritation in the respiratory system.

(3) *Irritant smokes:* sternutators [3] that can be disseminated in air as extremely small solid (or liquid) particles.

(4) *Lachrymators:* irritants that cause a copious flow of tears and intense though temporary eye irritation.[4]

War gases may be further classified as persistent or non-persistent according to their rate of volatilization, likelihood of dispersion by air currents, or their destruction by hydrolysis when dispersed. This quality is a major factor governing their tactical use; non-persistent agents, such as phosgene, would be employed against positions to be attacked shortly afterward, whereas persistent agents, such as mustard gas, would be used to harass the enemy or render positions untenable. A list of the war gases is presented in Table 128, together with pertinent information about each. Examination of the chemical formulas and the raw materials required will suggest the processing steps used in their manufacture. Some of these are described in more detail below.

There are several methods of dispersing war gases, the choice depending largely upon the tactical situation. High-explosive shells, the 4.2-inch chemical mortar, the Livens projector (usually a one-shot mortar installed in batteries of 25 and fired simultaneously), aerial bombs, aircraft spray, chemical cylinders or "candles," hand grenades, and even land mines may be used to project or disperse these chemicals. The 4.2-inch mortar had an interesting history in World War II. Developed by the Chemical Warfare Service, this portable mortar has a *rifled* barrel which gives the shell a long range and extreme accuracy. It is capable of rapid fire (in excess of 20 rounds per minute), and the latest model is recoil-less; some of the gas pressure generated by the burning propellant charge is allowed to escape through a large reaction chamber with an opening to the rear, thus balancing the momentum of the forward-projected shell. The advantages of such a weapon for projecting high-explosive shells was immediately apparent, and the gun

[3] A sternutator is any irritant which, when breathed in extremely low concentration, causes coughing, sneezing, or headache, followed by nausea and temporary physical disability. After removing the mask, the soldier is vulnerable to poison gas.

[4] These definitions are quoted from the U. S. War Department Technical Manual, "Military Chemistry and Chemical Agents" TM 3-215, 1940, page 84.

TABLE 128.—*War Gases.*

Common Name	C.W.S. Symbol	Chemical Name	Chemical Formula	Persistency[a]	Usual Raw Materials	Neutralizing Agents: Field	Neutralizing Agents: Gas Mask
			Lung Irritants				
Chlorine	Cl	Chlorine	Cl_2	10 minutes	NaCl brine; eletrolysis.	Alkali.	Type A Carbon and soda-lime.
Chloropicrin	PS	Trichloro-nitromethane	$Cl_3C \cdot NO_2$	6-12 hours	Picric acid, chlorine.	Na_2So_3 in alcohol.	Type A Carbon.
Phosgene	CG	Carbonyl chloride	Cl_2CO	10-30 minutes	CO, Cl_2; carbon catalyst.	Alkali; steam.	Type A Carbon and soda-lime.
Cyanogen chloride	CK	Cyanogen chloride	ClCN	10-30 minutes	NaCN *aq.*, Cl_2.		Type ASC Carbon.
			Vesicants				
Mustard gas	HS	*Bis*-2-chloro-ethyl-sulfide	$(ClCH_2 \cdot CH_2)_2S$	1-7 days	C_2H_4, S_2Cl_2.	Hypochlorites; 3% Na_2S sol'n.	Type AS Carbon.
Lewisite	M-1	*Beta*-chlorovinyl-dichloro-arsine	$ClCH:CH \cdot AsCl_2$	1-7 days	$AsCl_3$, C_2H_2; $HgCl_2$ catalyst.	Alcoholic NaOH.	Type AS Carbon.
Ethyldichloro-arsine	ED	Ethyldichloro-arsine	$C_2H_5 \cdot AsCl_2$	1 hour	$AsCl_3$, C_2H_6; catalyst.	Aqueous NaOH.	Type AS Carbon.
			Irritant Smokes				
Adamsite	DM	Diphenylamine-chloro-arsine	$C_6H_4(NH)AsCl \cdot C_6H_4$	10 minutes	Diphenylamine, $AsCl_3$; catalyst	Bleaching powder solution.	Filter.
			Lachrymators				
Chloroaceto-phenone	CN	Phenyl-chloro-methyl-ketone	$C_6H_5 \cdot CO \cdot CH_2Cl$	10 minutes	Chloroacetyl-chloride, benzene; $AlCl_3$ catalyst	Strong, hot Na_2CO_3 solution.	Type A Carbon, filter.
Brombenzyl-cyanide	CA	Bromobenzyl-cyanide	$C_6H_5 \cdot CHBr \cdot CN$	several days	Benzyl cyanide, bromine.	Alcoholic NaOH.	Type AS Carbon.

[a] Persistency varies with summer and winter, and with other factors.

[b] In civilian and industrial masks; combat masks use Type AS or ASC Carbon, and no soda-lime is needed.

was soon in use not only by ground troops but also in amphibious naval craft. It proved particularly effective in countering enemy mortar fire during the establishment of beachheads before the landing of artillery.

Gas Mask and Gas Adsorbents

For protection against war gases, men and animals must depend on the chemical adsorbents and the filter contained in gas-mask canisters. (In the case of the vesicants, impregnated garments and special shoes must be worn, to cover the whole body.) Until 1942, two chemical adsorbents were used separately, in series: (1) a copper-impregnated activated carbon called Type A or Whetlerite carbon; and (2) soda-lime. The latter is a mixture of hydrated lime (adsorbent), Portland cement (for hardness), kieselguhr (for bulk), and caustic soda (to increase the activity of the lime). The mixture is granulated and sprayed with a solution of sodium permanganate, which oxidizes arsine and similar compounds.

Charcoal may be activated by several processes, in each of which it is of primary importance to produce a skeletal carbon which has a multitude of very fine pores (micropores). In one method, peat is mixed with zinc chloride, and calcined in a muffle at 700° C. or just below. In another method, a hardwood in chip form is carbonized in a rotary kiln at 400° C., followed by steam treatment at 900° C. These products have a high adsorptive capacity for gases, and act in the gas mask canister to remove the chemical agents as condensed liquids or adsorbates. For greater effectiveness against a wider range of poisons, the activated carbon must be impregnated with copper sulfate, either alone or in combination with potassium hydroxide, pyridine, or silver nitrate, which act catalytically to decompose arsines and hydrogen cyanide particularly.

The development in 1942 of Type AS carbon eliminated the need for soda-lime, and the further development of Type ASC carbon in 1943 provided protection for the first time against cyanogen chloride; these new carbons contain additional and still secret impregnants.[5]

Processes of Manufacture

The manufacture of *chlorine* from sodium chloride brine is described in detail in Chapter 5. It is not very toxic compared to the other war gases and protection against it is relatively easy. Its principal importance to chemical warfare is in the manufacture of other agents. *Phosgene* results from the combination of carbon monoxide and chlorine in the presence of carbon granules. The reaction is carried on in two stages since a great deal of heat is evolved; in the first reactor—a cast-iron chamber filled with catalyst and thoroughly cooled by cold water—the conversion takes place to about 80 per cent, while in a second chamber it is completed at a higher temperature. The gaseous phosgene is dried in sulfuric acid towers, and then liquefied by passage through refrigerated coils. Excess carbon monoxide is used; this

[5] "Report of Activities of the Technical Division During World War II," by E. R. Baker, published by the Army Service Forces, Office of the Chief, Chemical Warfare Service, Washington, D. C. (1946), p. 174. This publication describes the most recent advances in this field and will be referred to frequently in this chapter.

does not liquefy, and is vented at the discharge point, where the liquid phosgene is run into iron containers previously evacuated and cooled. Phosgene is a commercial chemical used in organic reactions, for example, in the manufacture of acetyl chloride and certain ketones.[6]

Chloropicrin is now made by the reaction of chlorine and picric acid (symmetrical trinitrated phenol), or by the older process of passing steam through a mixture of calcium picrate and bleaching powder ($CaOCl_2$).

Cyanogen chloride (ClCN) is a very toxic low-boiling liquid which was not highly regarded as a war gas prior to World War II because of its instability in storage (cyanuric chloride being formed by polymerization). Discovery that the Japanese troops were issued glass grenades filled with hydrogen cyanide, however, prompted research which culminated in the use of sodium pyrophosphate as a stabilizer, so that this agent could be used if necessary. At the same time, a new impregnant for the charcoal adsorbent used in gas masks had to be developed. Cyanogen chloride is made by the action of chlorine on an aqueous solution of sodium cyanide followed by condensation of the slightly water-soluble gas:

$$Cl_2 + NaCN \rightarrow ClCN + NaCl$$

In peacetime, it is used with hydrogen cyanide (HCN) in fumigating ships and warehouses. The lachrymatory effect of cyanogen chloride gives warning of the toxic atmosphere.

Mustard gas is made by passing ethylene into sulfur monochloride:

$$2C_2H_4 + S_2Cl_2 \rightarrow (CH_2ClCH_2)_2S + S$$

The free sulfur formed is retained in colloidal suspension for the most part if the reaction is run at 30° C.; the difficult operation of removal is thus avoided. The product containing colloidal sulfur is nearly, if not quite, as active as pure mustard gas. In the Levinstein process, the reaction takes place in the presence of mustard gas from a previous batch, which acts as a solvent. The product is run to settling tanks, where a small amount of sulfur and sludge settle out; the heavy, dark, oily liquid is drawn off ready for shell filling. Pure mustard gas has a melting point of 58° F.; the product made as described contains impurities which lower the melting point to 46-50° F. Purification by vacuum distillation has recently become standard practice; this removes most of the odor of mustard or horseradish[7] which otherwise serves to identify the agent. Hexamethylenetetramine is added to increase its stability in storage.

Sulfur monochloride, a liquid, is made by bubbling dry chlorine gas through molten sulfur; the process is carried on in horizontal steel cylindrical tanks, which are cooled by means of an external water spray after the reaction starts. $2S + Cl_2 \rightarrow S_2Cl_2$. Ethylene is available in large quantities from petroleum cracking: in emergencies, it may be prepared conveniently by passing alcohol vapors over kaolin heated to 500° C.: $C_2H_5OH \rightarrow C_2H_4 + H_2O$.

[6] "Phosgene as a raw material for new chemicals," *Chem. Ind.*, 61, 805 (1947).

[7] The odor of this agent gives it its name. It is not related chemically to the true, natural mustard oil obtained from the seeds of black mustard, which is allyl-isothiocyanate ($CH_2{:}CH{:}CH_2N{:}C{:}S$).

Lewisite, a vesicant in good repute at the end of World War I, was studied intensely during the recent war, and abandoned as not sufficiently useful.

Chloroacetophenone, a solid, is produced from acetic acid, chlorine, and benzene. Acetic acid is chlorinated to form monochloroacetic acid, ($CH_2Cl \cdot CO \cdot OH$); this compound is then treated with chlorine and sulfur monochloride to form chloroacetylchloride ($CH_2Cl \cdot CO \cdot Cl$). The final step is the treatment of chloroacetylchloride with benzene in the presence of aluminum chloride to form chloroacetophenone ($C_6H_5 \cdot CO \cdot CH_2Cl$). The properties of this agent can be improved by making a mixture of chloroacetophenone, chloropicrin, and chloroform (Symbol CNS), which has a persistency of 1 to 6 hours. Another mixture, called CNB, contains chloroacetophenone, carbon tetrachloride, and benzene; it is used for training purposes because its action is less severe than CNS.

Bromobenzylcyanide manufacture consists of the following steps: benzyl chloride ($C_6H_5 \cdot CH_2Cl$), made by chlorinating toluene at 100° C., is mixed with an equal volume of 50 per cent alcohol and treated with sodium cyanide, forming sodium chloride and benzyl cyanide ($C_6H_5 \cdot CH_2CN$). The cyanide is subjected to fractional distillation and the fraction boiling within 3 degrees of the boiling point (231.7° C.) is treated with bromine vapor mixed with air; the reaction is catalyzed by a small amount of bromobenzylcyanide from a previous batch. The product ($C_6H_5 \cdot CHBr \cdot CN$) is freed by a stream of air from the hydrogen bromide formed at the same time, and is then sufficiently pure to be used as a lachrymator. It has a low vapor pressure and is thus highly persistent.

The use of "tear gas" by public officers to control mobs and riots without the use of firearms is now common practice. The lachrymator is usually chloroacetophenone, or a mixture of that agent with Adamsite (diphenylaminechloroarsine), which produces a sickening effect.

Screening Smokes

Chemicals in this category are those which when dispersed in air produce a cloud of finely divided particles of solid, liquid, or both. These are used to shield tactical operations or disrupt the movements of the enemy. Several are known; the outstanding examples are listed in Table 129, together with a description of their composition, reaction products, and screening effect. The latter is usually designated as "T. O. P.," or total obscuring power, a unit expressing the square feet of cross-sectional area of the completely obscuring cloud formed by one pound of smoke-producing material.[8] It is not the total amount of light passing through a cloud which is important, but the percentage of undeflected rays; a white cloud obscures better than a black one because of the greater reflectance of the particles.

It is of interest to note the change that occurred in the HC mix during World War II. Until 1942, this screening smoke was composed of hexachloroethane, zinc powder, and potassium perchlorate, ammonium chloride being added to control the burning rate, and calcium carbonate to stabilize the mixture (against moisture absorption). A shortage of perchlorate forced

[8] After Baker, *op. cit.*, p. 55.

a change to sodium nitrate, which proved exceedingly sensitive to moisture; as a result, fires broke out in storage. A different formulation using calcium silicide was tried, but the silicide proved too difficult to grind, because of its hardness. Finally a mixture was found which was better in many ways than the original; it is a combination of hexachloroethane, aluminum, and zinc oxide. This requires no stabilizer, and changing the percentage of aluminum varies the burning time as desired. The substitution of zinc oxide for zinc was helpful in several ways. The reaction involved when the mix is ignited (as from a "candle") may be visualized in two parts:

$$3ZnO + 2Al \rightarrow Al_2O_3 + 3Zn$$
$$3Zn + CCl_3 \cdot CCl_3 \rightarrow 3ZnCl_2 + 2C$$

The alumina, zinc chloride, and carbon particles so formed all contribute to the obscuring power of the smoke.

Of the other chemicals listed, sulfur trioxide (in chlorosulfonic acid) and titanium tetrachloride upon dispersal react with the moisture in the air to form hydrolysis products, as indicated in Table 129, which provide the screening effect. White phosphorus reacts directly with the oxygen in the air to form phosphorus pentoxide in the form of very finely divided white particles; its reaction with the moisture in the air to make meta- or ortho-phosphoric acid occurs mainly after extreme dilution, and is of minor importance. The FS and FM smokes can be dispersed by nearly any means, including airplane spray, while WP requires shell-loading with a bursting charge to scatter the phosphorus into the air.

The floating smoke-pot used by naval craft and for screening harbors and beaches is completely waterproof and will evolve HC mixture for a period of 10 to 20 minutes. A similar smoke-pot is used in connection with land installations to provide a screen on short notice until the large fog generators are functioning at full capacity.

These "artificial fog" generators are a recent development.[9] Their principle is essentially that of steam-distillation of fuel oil. The resultant low-hanging cloud is dense white with very effective screening properties. A truck-mounted generator can blanket a square mile area within 10 minutes.

Used to identify ground troops and armored vehicles to friendly aircraft, and for signalling, *colored smokes* consist of mixtures of chemicals which produce a white smoke with, for example, various anthroquinone dyes which provide a wide range of colors.

Incendiaries

Incendiary bombs are of several types, differing from one another in type of filling, metal used for the case, size, and action upon ignition. Wisely used in World War II was the four-pound bomb with a hexagonal magnesium body, 21 inches long, filled with "thermate" mixture and ignited by a primer composition which gives a long, hot flash. On burning, pieces of molten magnesium might be hurled as far as 50 feet.

A six-pound bomb with a steel case 19 inches long contains a cheesecloth sack filled with jellied gasoline which is thickened with "Napalm." A black-

[9] Baker, *op. cit.*, p. 151.

TABLE 129.—*Screening Smokes.*

Common Name	C.W.S. Symbol	Chemical Components	Primary Reaction products when released in air	"T.O.P." Value[a]
White phosphorus	WP	White or yellow phosphorus.	Phosphorus pentoxide (P_2O_5)	3,500
Sulfur trioxide mixture	FS	sulfur trioxide SO_3 (55%) chlorosulfonic acid ($ClSO_2OH$) (45%)	hydrochloric acid (HCl) sulfuric acid (H_2SO_4) (moisture required)	2,240
Hexachloriethane (or HC) mixture	HC	hexachloroethane ($CCl_3 \cdot CCl_3$). aluminum powder Al zinc oxide (ZnO).	zinc chloride ($ZnCl_2$) carbon aluminum oxide (Al_2O_3)	2,000 (?)
Titanium tetrachloride	FM	Titanium tetrachloride ($TiCl_4$).	titanium hydroxide [$Ti(OH)_4$] hydrochloric acid (HCl) (moisture required)	1,900
Artificial fog		Steam and fuel oil vapors	Steam and fuel oil condensed droplets	Not published
Crude oil	CO	Mixture of hydrocarbons	Colloidal carbon [b] (by partial combustion)	200

[a] From War Dept. Technical Manual TM 3-215 p. 136. A standard smoke is one of such density that a blanket of smoke 100 feet thick completely blots out the light from an electric lamp of 25 candlepower.

[b] This is the only smoke in the list which is black; the rest are white.

powder charge expels the burning fuel as from a mortar, for a distance of about 75 yards.

Another famous filling, called "goop," is expelled from a 10-pound bomb in the same manner, by means of a black-powder charge; the finely divided magnesium present in this thickened gasoline filling not only provides heat, but leaves a hot, glowing ash which radiates heat downward. These small bombs are dropped in clusters, either "quick-opening" to provide a scatter pattern to cover a wide area or "aimable" for pin-point attacks. A certain percentage of bombs in a cluster include a high-explosive or white phosphorus charge to discourage fire fighters. The effectiveness is further increased by the use of delayed fuses which permit penetration before ignition occurs.

Singly jettisoned bombs up to 500 pounds in size may be filled either with the "Napalm" or the "goop" mixture. The largest incendiary bomb was the 1100-pound "fire bomb" filled with thickened gasoline and ignited by means of a 4-pound magnesium bomb strapped to it; it could splash flame over an area the size of a football field.

One of the smallest air-borne incendiaries was the "bat incendiary," reportedly tested but never used. This 17-gram unit was to be strapped to a bat, which would then be dropped from an airplane at night over a city, to find its way into various inaccessible spots. The jellied gasoline filling would be ignited by means of a match-head composition when the bat attempted to relieve itself of the incendiary capsule.

Flamethrowers such as pictured in Fig. 243 are devices from which gasoline thickened with "Napalm" can be projected for ranges up to 75 yards with nearly pin-point accuracy,[10] while shorter, bushy flames can be obtained if unthickened gasoline or Diesel fuel is used. Portable one-man units are pressured with refillable tanks of compressed air or nitrogen, while in the most recently developed tank-mounted flamethrowers, the fuel is expelled by a motor-driven gear pump. Ignition of the fuel as it leaves the nozzle may be accomplished in several ways, for example by means of burning gasoline supplied by an auxiliary nozzle and ignited by an electric spark as the trigger is pulled.[11]

"Napalm" is a mixture of the aluminum soaps of naphthenic acid, coconut fatty acids, and oleic acid. It is prepared by coprecipitation from a mixture of the sodium soaps of these acids, by the addition of iron- and manganese-free alum. The stringy gel is then dried to a carefully specified low moisture content. For field use, it is hot-packed (melted) in metal containers, with *alpha-napthol* being added as an oxidation inhibitor. It can be mixed readily with 80-octane gasoline to produce "*thickened fuel*," or jellied gasoline; the viscosity of the fuel varies with the percentage of "Napalm" used: 4 per cent in flamethrower fuel, 6.2 per cent in the "fire bomb," and 9 per cent in the six-pound aerial bomb previously described. Other additives for thickening

[10] More highly-compounded thickened fuels peptized with cresylic acids have a range up to 300 yards and burn with more vigor. Baker, *op. cit.*, p. 48.

[11] This method has been superseded by a revolver-type nozzle which contains five cavities filled with a thermite composition containing a proportion of finely divided magnesium. The incendiary cavities are fired in rotation, as needed, by means of a firing pin striking a match-head composition. The glowing magnesium particles travel with the jet of fuel, insuring ignition. Baker, *op. cit.*, p. 148.

gasoline include *isobutyl methacrylate*, which is used in conjunction with sodium or calcium soaps, and *synthetic rubber* (GR-S), which is first dispersed in straight-run gasoline, then vulcanized by the addition of sulfur monochloride to give a tough, elastic fuel.

"*Pyrogel*," or "goop," is a dispersion of very fine particles of metallic magnesium in a matrix of asphalt. This material results during one of the steps in the production of magnesium by the Hansgirg process (Chapter 18). It can be mixed with approximately equal parts of gasoline thickened with

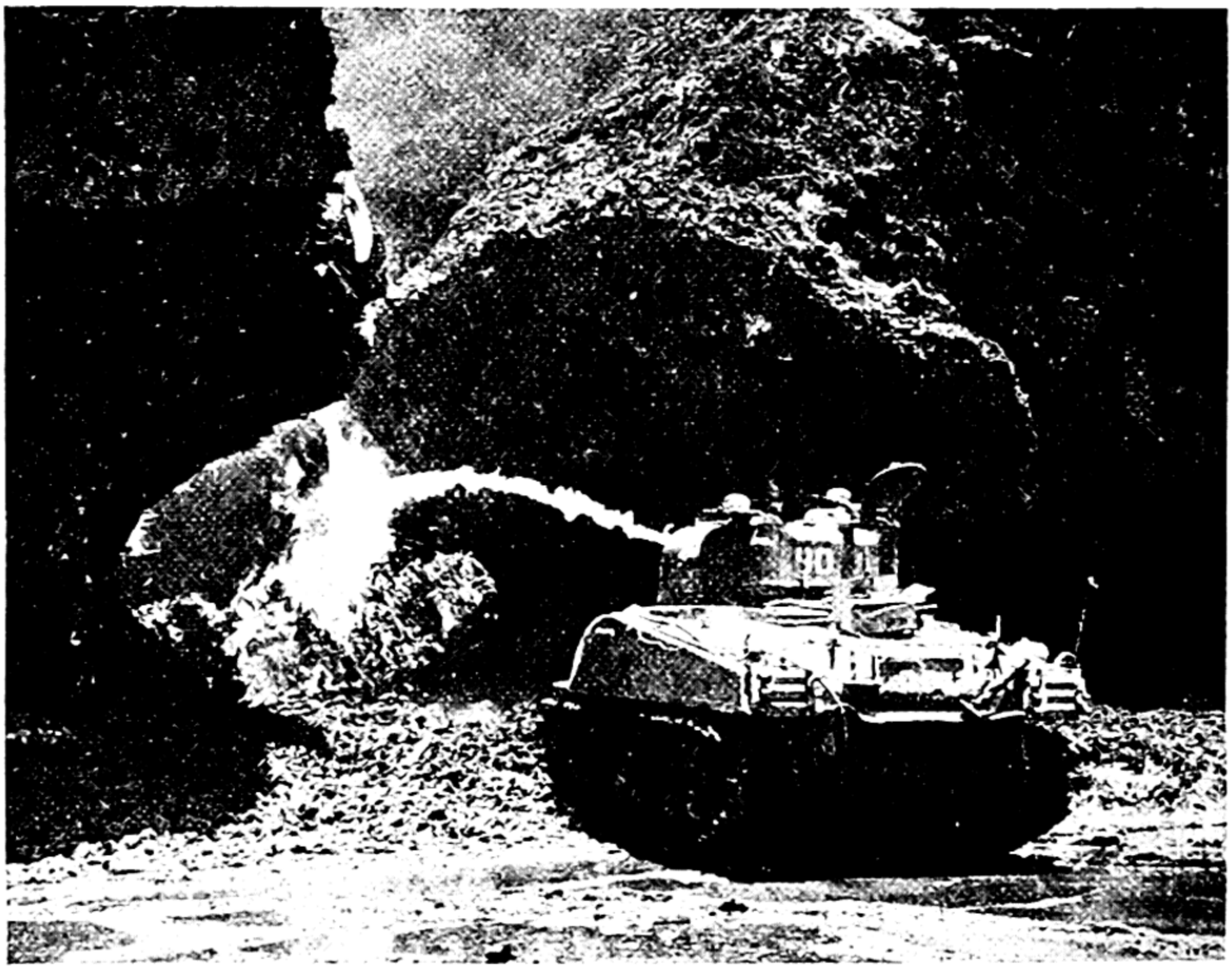


FIGURE 243.—A flame-throwing tank engulfs the entrance of a cave with fire on Okinawa. Many such caves fringed the southern shores of the island. Note the lance-like jet of fire. (Photo by U. S. Army Signal Corps.)

isobutyl methacrylate plus small amounts of oxidizing agents and certain oils to make an incendiary filling which is whitish in color and somewhat resembles cold-cream. A quite similar incendiary may be made by dispersing finely powdered magnesium-aluminum alloy in the synthetic rubber-sulfur monochloride gel.

A mixture of flaked aluminum, iron scale (hematite) and barium nitrate, which may be mixed with petroleum oil, is called "*thermate*." Used in magnesium bombs, when ignited by the primer it produces a temperature of 4500° F., higher than any other incendiary, according to the reaction:

$$3Fe_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Fe + \text{heat (the "thermit" reaction)}.$$

The barium nitrate is an oxidizing agent which aids in starting the reaction. This mix is also used in "thermit bombs," which are quite similar to mag-

nesium bombs except for the case, which is steel. These are not considered as effective as magnesium bombs since the case does not burn violently by itself as does the magnesium case.

General

"Doron"

Among many other successes of the Chemical Corps there should be mentioned the protective body armor named "Doron." It consists of sixteen layers of glass fiber woven cloth impregnated with a thermosetting resin, and bonded (by heat) under low pressure. It is fitted into exterior pockets in garments for our amphibious forces, in flak suits for aviators, and life preservers for Navy personnel; it is light, and strong enough to resist a shell splinter or stray piece of metal; it will not ordinarily stop a direct hit.

The Reuben Electric Cell

For the Handie-Talkie, and perhaps also for the Walkie-Talkie, there were needed extremely compact dry cells with a flat discharge curve, and a relatively high current. Such a cell is the alkaline dry-cell battery "Reuben," an alkaline zinc-mercury cell,[12] with a rated capacity of 200 milliampere-hours per each 1.6-gram unit of active material. Open circuit voltage is normally 1.34. The service obtainable from the Reuben cell is approximately 4 to 7 times that of the conventional dry cell of equivalent volume. The roll anode cell went into large-scale production for the Signal Corps during the war; it was produced at the rate of one million per day. The pressed powder anode cell structure gives additional volume reduction for a stated watt-hour capacity, and may be the selection for civilian use. It may serve also in miniature battery-powered electronic equipment. The smallest cell is circular, 0.610 inch in diameter and 0.533 inch high; 18 such cells are assembled, making a stick which resembles a fountain pen; four such sticks make up the BA-38-R battery, the B battery for the Handie-Talkie radio set.

Reading References

"Chemistry in World War II," edited by D. A. Noyes, Jr., Little, Brown and Company, Boston, 1948.

"The chemist's military horizon," Robert P. Patterson, *Chem. Eng. News*, 24, 1029 (1946).

"The Chemical Warfare Service in World War II," by U. S. Army Chemical Corps, Reinhold Pub. Corp., New York, 1948.

"Tabun, the gas that drives men mad," Ladislas Farago *United Nations World*, p. 11, February, 1948.

"Various chemical mixtures used in CWS fire bombs," *Chem. Ind.*, 57, 79 (1945).

"Chemical smokes and smoke screens," H. A. Levey, *Chem. Ind.*, 58, 980 (1946).

"Gelled fuel for flame throwers," Dr. C. M. Cauley, *Industrial Chemist*, 22, 150 (1946).

"Napalm," L. F. Fieser, G. C. Harris, E. B. Hershberg, M. Morgan, F. C. Novello and S. T. Putnam, *Ind. Eng. Chem.*, 38, 768 (1946).

"Chemical Warfare on Bataan and Corregidor," Alfred F. Torrisi, *Chem. Eng. News*, 25, 2557 (1947).

"Rocket propulsion," W. H. Wheeler, *Industrial Chemist*, 24, 250-8 (1948).

[12] "The Reuben cell—A new alkaline primary dry cell battery," Maurice Friedman and Charles E. McCauley, the Electrochem. Soc., Boston meeting, preprint 92-6, p. 81-100. U. S. Pat. 2,422,045 and -6 (1947), to S. Reuben.

The history of synthetic plastics begins with the invention of Celluloid, in 1869, by John Wesley Hyatt and his brother Isaiah. After a lull of forty years, another fundamental invention was made: Dr. Leo Baekeland, recently come to America from Belgium, invented and produced the first of the phenolformaldehyde resins, and from it the first heat-set plastics. A third big date is 1923, when Fritz Pollock and Kurt Ripper invented "Pollopas," the first ureaformaldehyde resin. Numerous other inventions have been made in territory which, chemically speaking, might be called adjacent. Keeping step with the inventions have been improvements in the engineering equipment, in procedure, and in the applications of resins and plastics. So great and rapid have been the developments that the preparation and application of synthetic resins and plastics was a billion dollar industry in 1949.

Chapter 35

Synthetic Resins; Synthetic Plastics

Chemical Nature

Synthetic plastics are synthetic organic materials which are rigid in their final, useful form, but which at some stage of their manufacture, under the influence of heat, were plastic, and while in that state, were given their final shape under the influence of pressure. Synthetic resins are the materials from which the synthetic plastics are made. To a considerable degree, the terms are interchangeable; they have a meaning when there is a chemical change in the transition of resin to plastics, with accompanying changes in the physical properties, as in the molding of thermosetting resins. In the molding of thermoplastic resins, there is no chemical change, and no change in physical properties; nevertheless, the granules forming the material about to be molded are termed "the resin."

The two main groups of synthetic resins destined to become plastics differ radically. The thermosetting resin is molded under heat and pressure, and held in the heat until set, that is, until its final rigid state has been reached; it is then cooled, and should it be reheated, it will not soften. Hence its set is irreversible. The thermoplastic resin is also molded under heat and pressure, but it must be chilled in order to harden it, so that it may retain its molded shape for useful purposes. It may be said to be "cold-set." Should it be reheated, it will soften again, and may be shaped anew. To express the distinction in another way, the process of thermosetting is irreversible, while the process of thermoplasticizing is reversible. It follows that for the manufacture of a molded article which will be exposed to heat, a thermosetting plastic is the proper selection, for it will resist the heat to a certain degree, whereas the thermoplastic article similarly exposed will soften considerably.

The resin may be molded by itself, without filler; this results in a 100 per cent resin molding, which may be not only transparent but also absolutely free from color. Several resins owe their usefulness to this property [methylmethacrylate ("Plexiglas," "Lucite"), polystyrene]. A number of

resins in molding materials, especially the thermosetting resins, are generally mixed with an appreciable percentage of a filler, such as wood flour, cellulose, cotton flock, asbestos, carbon black, mica, or others, which modify the properties of the final product. Still other resins are so compounded and treated in the process of manufacture that they are oil-soluble, and otherwise suitable for incorporation in protective coatings. Other resins, again, are of value as laminating agents, as adhesives, and in still different ways. The relative importance of the several kinds of resins is indicated in Table 130.

TABLE 130.—*Production of plastics materials, grouped according to use (1947).**

Synthetic organic plastic materials	Pounds	Value per pound
For protective coatings	453,006,000	$0.33
For molding and casting	312,737,000	.36
For laminating	45,866,000	.32
For adhesives	98,346,000	.27
For treatment of textiles, paper, and leather	54,251,000	.39
For ion exchange	7,874,000	.25
For miscellaneous uses†	279,620,000	.53
Total	1,251,699,000	.38

* U. S. Tariff Commission Report.
† Includes glazing, film, and sheeting.

Synthetic resins may be the products of condensations, that is reactions which involve the formation and elimination or "splitting out" of a molecule of water (or other simple substance) from two different molecules, followed by the union of the two large remainders; or they may be the product of polymerization at the double bond unsaturation. In the latter case, there is no elimination of any substance. In general, the products of condensation are thermosetting resins, the products of polymerization thermoplastic.

The following are the important groups of synthetic resins exclusive of certain oil-soluble resins, textile and paper-treating resins and adhesives.

Thermosetting resins, formed by condensations

Phenolformaldehyde, cresolformaldehyde ("phenolics")
Ureaformaldehyde, thioureaformaldehydes ("amino resins")
Melamine-formaldehyde ("melamines")
Phthalic anhydride-glycerol and pentaerythritol, maleic anhydride-glycerol ("alkyds")

Thermoplastic resins, formed by polymerization

Polyvinyl chloride, acetate, and copolymers, polyethylene or polythene, polyvinyledene chloride ("vinyl resins")
Polymethacrylate and methyl methacrylate ("acrylics")

Thermoplastic resins derived from cellulose

Cellulose nitrate, compounded to Celluloid, pyroxylene
Cellulose acetate, cellulose acetate butyrate, ethylcellulose

Many resins are known by their registered trade marks, and reference will be made to some of these. Others are known by their chemical names, prefaced by the manufacturer's name or a registered designation; thus there is a Bakelite phenolic resin, but also a Bakelite polystyrene, a Bakelite polyethylene, and others. "Lustron" and "Styron" are definite designations

for polystyrene. A more precise designation fixes the formula and color in addition to the kind of resin, by means of numbers and letters; examples are given later.

The number of resins on the market is great, and is still growing. A chart entitled "Plastics, resins and rubbers,"[1] contains 64 items, grouped as follows: Under condensation polymers, 24; under vinyl polymers, 23; under resins from rubber and synthetic rubber, 5; under plastics from cellulose, 9; under resins from rosin, 3.

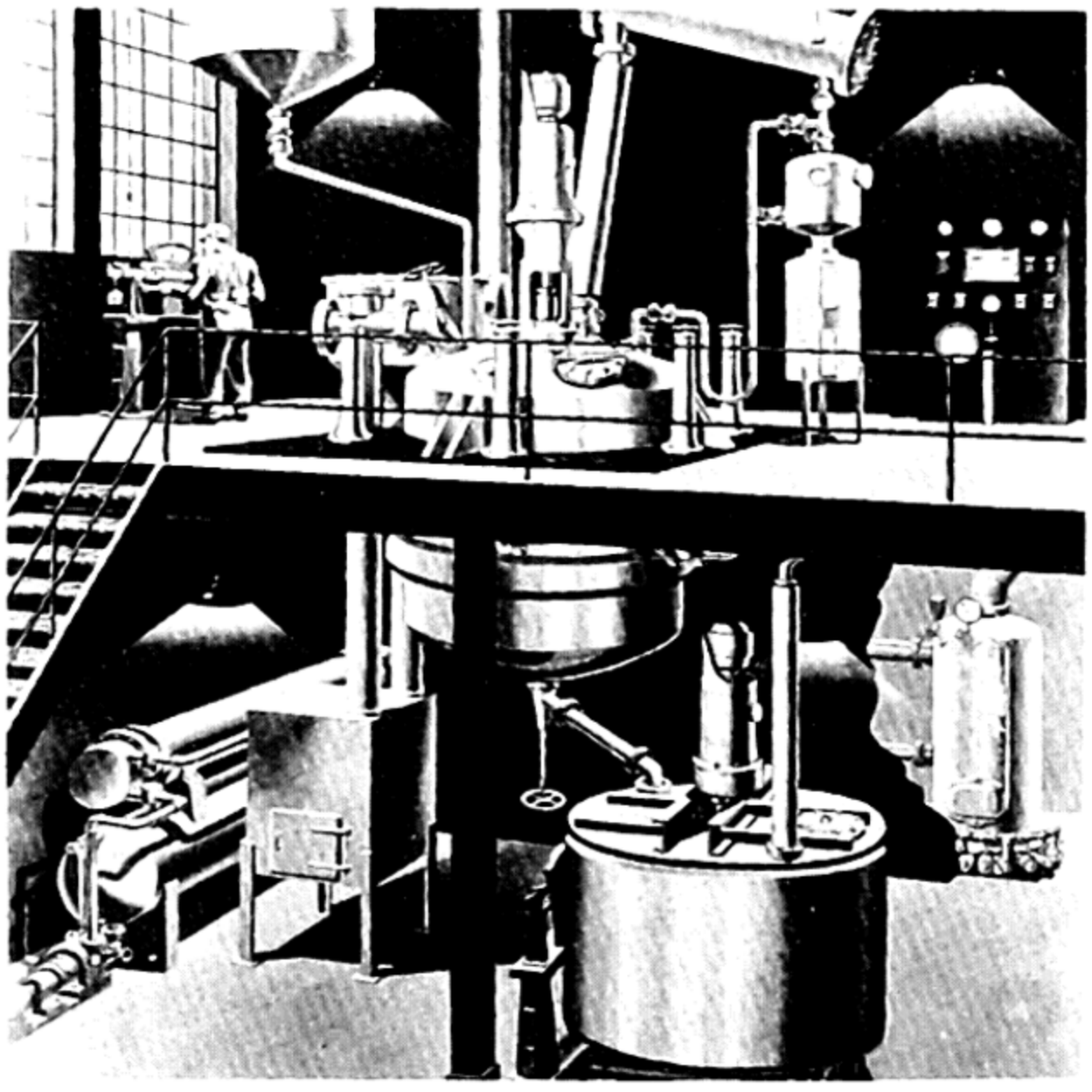


FIGURE 244.—A synthetic resin production plant. (Courtesy of Blaw-Knox, Pittsburgh, Pa.)

THE MANUFACTURE OF SYNTHETIC RESINS

The manufacture of resins requires simple apparatus; the process consists as a rule in mixing two liquids, or a solid and a liquid, heating them together to produce the reaction, removing any water formed or part of it, then heating the product further with, or without, additions, until a test sample shows the proper melting point and viscosity. The end point is not definite, and a variety of intermediate products may be obtained. Uniform products are obtained only by taking the same quantities, heating to the same temperature for the same length of time, with all other conditions identical. Not only the length of cook, and temperature, but the absence, presence, and kind of catalyst influence the properties of the product.

The depth of color of the product depends partly on the degree of purity of the raw materials; in general, the darker these are, the darker will be the resin.

[1] "Plastics, resins, and rubbers," Paul O. Powers, *Chem. Eng. News*, 24, 2784-8 (1946).

In order to produce synthetic resins at reasonable prices, relatively inexpensive raw materials must be available. The chief raw materials are urea, formaldehyde, phenol, phthalic anhydride, glycerin, acetone, methanol, acetylene, styrene, acetic anhydride, and acetic acid. The resins containing phenol, cresol, or resorcinol, may be classed as of coal-tar origin, as may also the Glyptals made from phthalic anhydride, and those made with maleic anhydride. The noncoal-tar resins include the polyesters and the cellulosic group.

FIGURE 245.—Phenol-formaldehyde resin A being discharged from the reaction kettle. In two minutes, all of the floor visible in the picture is covered with resin. The warm mass is allowed to spread over the whole floor, is cooled, and then broken up and granulated. (Courtesy of Durez Plastics and Chemicals, Inc., Tonawanda, N. Y.)

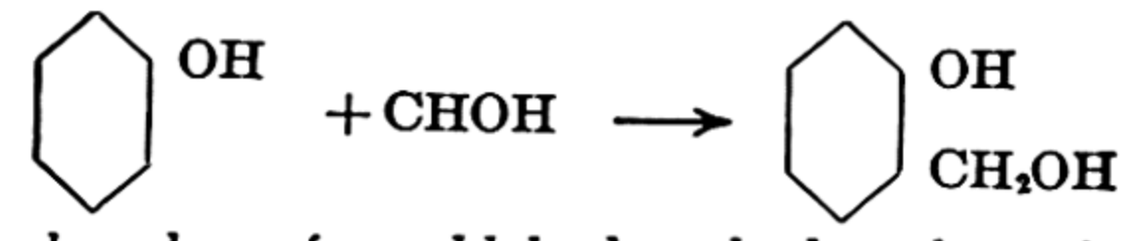
The tendency today is rather to distinguish between the benzenoid resins, which contain the benzene ring, and the nonbenzenoid resins, which do not.

Products of Condensations

Phenolformaldehyde Condensation Product. The first of the modern synthetic resins was the product of the condensation of phenol and formaldehyde. The phenol in liquid form [2] and the formaldehyde as a 30 per cent

[2] Phenol is a solid, melting at 40.8° C.; 2 per cent water liquefies it.

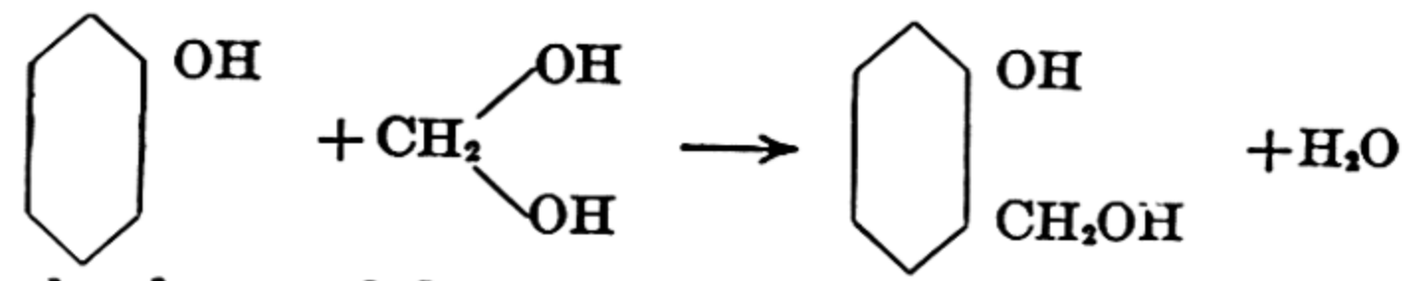
water solution, about equal parts by weight (see later), are placed together in a jacketed kettle fitted with a reflux condenser and an agitator; the two liquids are miscible. Then 0.5 to 5 per cent of a catalyst (on the weight of the phenol)—selected from a long list of materials—basic or acid, organic or inorganic—is added. At first, gentle heat is applied, until the reaction is well started. Later, in order to moderate the reaction, the kettle is cooled. After an hour or so, the upper water layer which gradually accumulates has reached a maximum, and is run off. The kettle is heated to a minimum temperature, a vacuum applied, and any residual water removed past the condenser from which the cooling water has now been turned off. The lower layer is a liquid at the kettle temperature; it is run off onto the floor where it hardens to an amber-colored brittle solid—the new resin, soluble in organic solvents. The reactions are:



phenol *formaldehyde* *hydroxybenzyl alcohol*

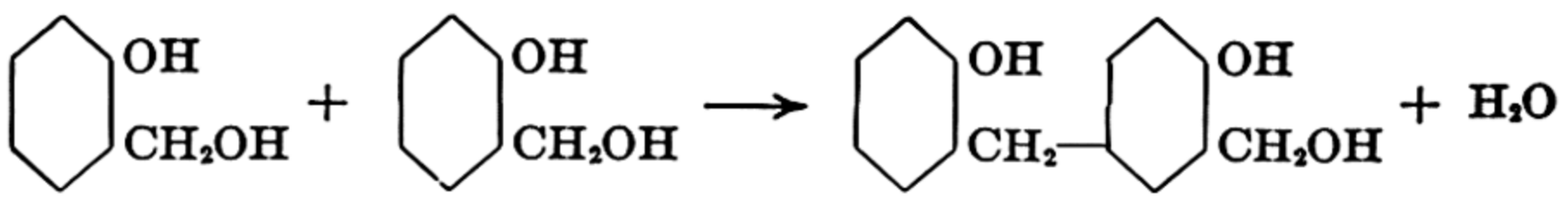
By writing formaldehyde in its hydrated and no doubt true form when in solution, as methylene glycol, the reaction is clearly shown to be a condensation reaction, and it becomes more understandable:

$$CHOH + H_2O \rightarrow CH_2(OH)_2, \text{ and}$$



phenol *methylene glycol* *hydroxybenzyl alcohol*

The hydroxybenzyl alcohol reacts further, lengthening the chain (see later), while at the same time cross-linking may be taking place:



The resin formed is resin "A," and is itself reactive upon being heated. There are two modifications in the procedure for its manufacture, developed by the early inventors and workers, and still in use.

In the "one-step" method, less than 1 mole of phenol is taken for each mole of formaldehyde; the catalyst added may be any alkali, including ammonia, caustic or barium hydroxide. The product from the kettle is the finished resin "A," which requires only to be broken, when cold, into fragments, and then powdered, ready for the mixer and blender.

In the "two-step" method, more than 1 mole of phenol is taken for each mole of formaldehyde; the catalyst added is acid, as for example hydrochloric or oxalic acid. The product from the kettle this time is not the curable resin, although it too hardens to a brittle solid. It may be called

"Novolac," and is reduced to a powder which must be mixed with a further amount of formaldehyde in the form of hexamethylenetetramine, and warmed with it, in order to approach the curable resin stage "A."

The "one-step" method is more critical; an overheat will cause a premature hardening to the final state "C." The "two-step" process is safer; the progress of the resin toward the final cure is under close control.

Molding Compound. For thermosetting resins in general, and the phenol-formaldehyde molding resin in particular, a filler is mixed with the resin, as well as a lubricant, an accelerator, and a color. For example, a typical phenolic molding powder would have the composition:

	By Weight
Resin (the binder)	48%
Filler	48
Lubricant	1.5
Accelerator	1.0
Color	1.5

American practice is to hold the resin at 45 per cent or higher. The filler may be wood flour; the color for black is carbon black, which may also be part of the filler. A second frequently selected color for phenolformaldehyde resin compounds and hence plastics is brown, produced by means of oxides of iron. The filler serves several purposes: it reduces shrinkage and brittleness; it improves impact strength, tensile strength and dielectric strength. Best of all, being relatively cheap, it lowers the price of the compounded resin.

The molding compound whose resin is still reactive must be "advanced," to a definite point in the intermediate state, so that when the customer places it in his presses, it will fully cure in a specified standard time. The "advancing" of the resin is done by running it between warm rolls over and over, and testing the rapidity of cure at intervals. In addition, batches are mixed and blended.

It is well to distinguish three distinct divisions among the industrialists who are concerned with the plastics industry:

(1) The resin manufacturers, who buy or make chemicals and bring them to reaction.

(2) The molder, who buys the molding compounds on specifications, in cardboard drums, ready for the presses.

(3) The assembler, who orders the moldings from group 2, and assembles molding, metal parts and others to produce the finished articles, such as a radio, or weighing scales.

The phenolformaldehyde condensation product may be adapted to uses other than making molding materials for plastics.

The "Novolac" obtained in the two-step process may be dissolved in organic solvents to produce a varnish which is employed in coating paper or fabrics, which are then piled on one another and hot-pressed to produce laminates, which are used for plates, panels, and gears.

Another aldehyde condensed with phenol is furfural. The method of manufacture is similar to that of phenolformaldehyde.[3] Phenolfurfural con-

[3] The process has been worked out by the Durite Corporation.

densation products are suitable for adhesives, impregnants and protective coatings, as well as for incorporation into molding materials.

On the other hand, other phenols are condensed with formaldehyde: cresol, and mixtures of simple phenol and cresols, reacted with formaldehyde, produce resins used with oils for protective coatings. Resorcinol-formaldehyde resins are in successful use in the form of waterproof adhesives which cure at room temperature.

By means of casting resins, *i.e.*, phenolics without filler which are furnished in the liquid state, true casting can be made. The casting will set at room temperature, or slightly above, if a certain amount of accelerator (for example, benzoyl peroxide) is added. A color can be incorporated. Castings which do not involve inner cores are the most successful.

Ureaformaldehyde Condensation Product. Ureaformaldehyde resin is made by reacting urea and formaldehyde in the presence of hexamethylenetetramine. The proportions may be 1 mole of urea to 1.5 or 2 moles of formaldehyde. The pH of the solution of urea in formalin is held between 5.5 and 8, depending upon the type of product to be made—whether a molded article, a resin for protective coating or an adhesive. The low pH promotes a high rate of reaction, and leads to a harder, more water-resisting molded product. The reaction is started with gentle heat, and proceeds briskly at 120° F. It is allowed to run until the methylol ureas, which were first formed, continue to combine by condensation reaction, reaching an intermediate stage in the growth of the polymer; it is stopped by cooling the resin in the reaction kettle. A part of the reaction water and solution water is removed by distillation at low pressure. When making the resin for the molding compound, the liquid from the kettle is filtered, and the clear filtrate, containing the resin, is mixed with 40 per cent (or so) pure cellulose (alpha cellulose) in a paste mixer. The mixed product is dried at low temperature, and is colored cold in a ball mill, with other additions, such as lubricants and catalyst. The reaction is as follows:

$$\begin{array}{l} NH_2 \\ | \\ C{:}O + CHOH \rightarrow \\ | \\ NH_2 \end{array} \begin{array}{l} NH_2{}^* \\ | \\ C{:}O \\ | \\ NH{\cdot}CH_2OH^{**} \end{array} \quad ; \quad \begin{array}{l} NH_2 \\ | \\ C{:}O + 2CHOH \rightarrow \\ | \\ NH_2 \end{array} \begin{array}{l} NH{\cdot}CH_2OH \\ | \\ C{:}O \\ | \\ NH{\cdot}CH_2OH \end{array}$$

urea (white solid) — *monomethylol urea* (a liquid) — *dimethylol urea* (a liquid)

Further growth of the molecule takes place with monomethylol urea, for example, when the amino group of one molecule (*) reacts with the hydroxyl (**) in the alcohol group of another, forming a molecule of water and the dimer. Further reaction takes place in the heat of molding. Like other thermosetting resins, urea resin sets to a hard, irreversible plastic.

The molding material, which contains the resin with the pure cellulose filler, is altered in the molding press to a translucent plastic, entirely free from color. It is used to a great extent as such for light reflectors. Most molding materials, however, are colored with dyes; indeed it is the main characteristic of urea resins that they may be colored any shade or tint

desired, no matter how delicate, without danger of fading (except by the dye itself). It may be added that urea plastics have an attractive surface gloss, and are fairly resistant to impact.

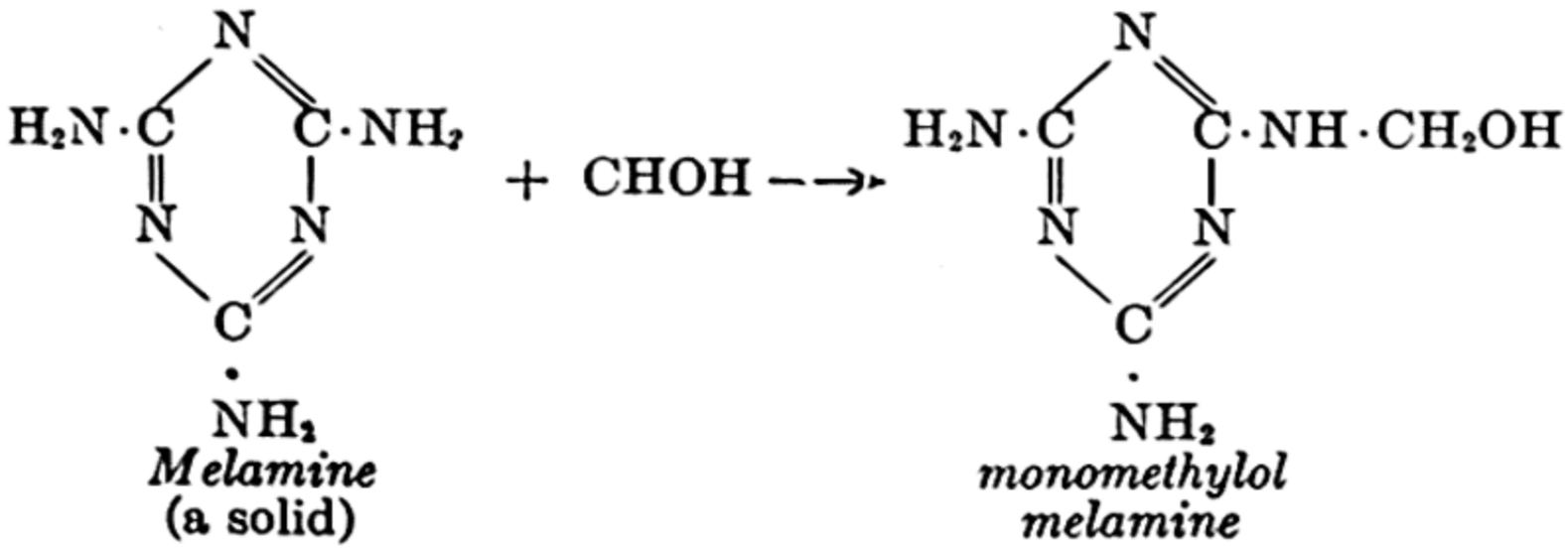
An equivalent weight of thiourea may be substituted for a part of the urea in batch formulation, resulting in an improvement in the molding characteristics and in increased resistance to water.

Melamine-formaldehyde Resins. Of great interest also are the melamine-formaldehyde, and melamine-urea formaldehyde resins and plastics, of comparatively recent development. Melamine $(H_2N \cdot CN)_3$ is made by heating dicyandiamide with ammonia under pressure; dicyandiamide is made, along with cyanamide, from calcium cyanamide:

$$CaN \cdot CN + H_2O + CO_2 \rightarrow H_2N \cdot CN + CaCO_3; 2H_2N \cdot CN \rightarrow HN:C \cdot NH_2$$

Calcium cyanamide — *cyanamide* — $NH \cdot CN$ *dicyandiamide*

The reaction of formaldehyde with melamine produces methylol melamine,



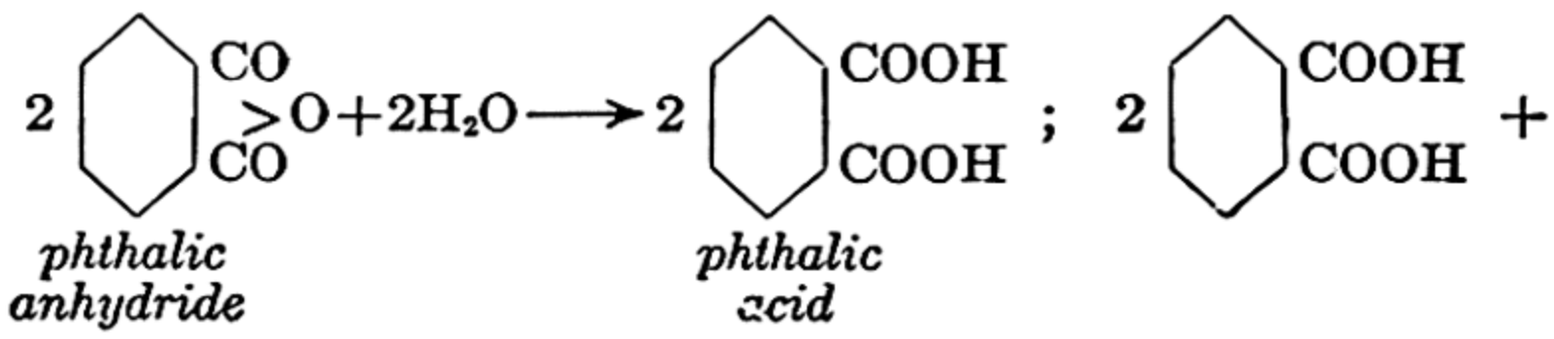
Melamine (a solid) — *monomethylol melamine*

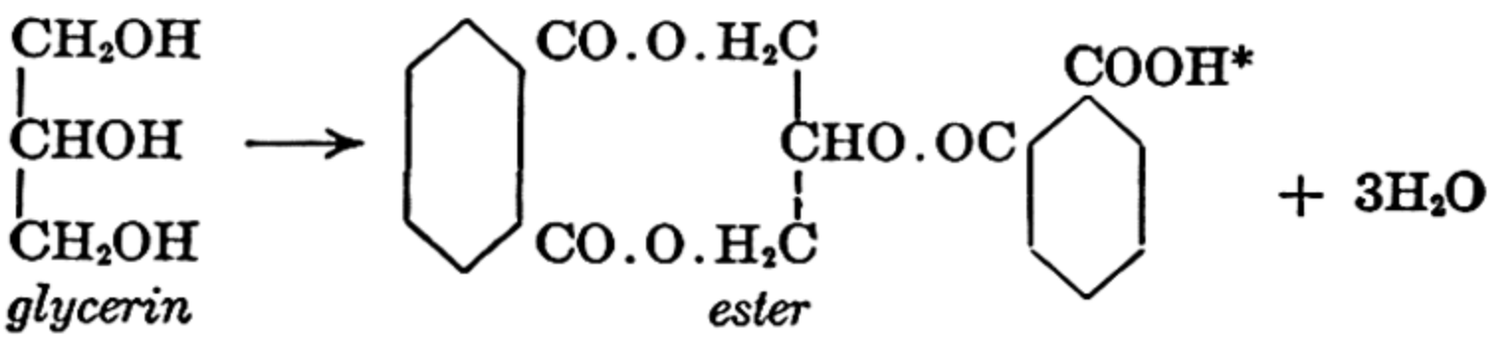
and higher methylols, which in turn combine, under heat, to give a condensation polymer in a way similar to the formation of the ureaformaldehyde polymer. The melamine resin is mixed with a filler in preparing the molding material. Urea and melamine together are made into a resin having certain special properties; also melamine may be alkylated first, as with butyl alcohol, and then reacted with formaldehyde.

Melamine plastics have a high surface hardness, superior to that of urea plastics, and a better water resistance. They are also less affected by electric arcing which is important in certain high-voltage applications.

Alkyd Resins. Alkyd resins are chiefly the condensation products of phthalic anhydride and glycerol (the phthalic alkyds), and of maleic anhydride and glycerol (maleic alkyds). The alkyds are thermosetting resins, but are not used for the manufacture of plastics by molding; they serve mainly in protective-coating compositions, which may be either air-drying or heat-drying (baking enamels). The mode of operation is generally as follows: 2 parts of phthalic anhydride and 1 part of glycerin together with a fatty acid or a selected vegetable oil, are heated together in a kettle in an inert atmosphere. The water of reaction is distilled off, and the resin combined with air-drying oils; or if a baking enamel is desired, with a urea- or melamine-formaldehyde resin. The baking enamel is sprayed onto the object, such as an automobile body, and is set by baking in an oven. Infrared lamps are successfully used for such baking. (Compare Chapter 31.)

Phthalic anhydride 2 parts and glycerin 1 part, heated together at 212° F., give a white liquid. On further heating to 365° F., a distillation takes place; when this is over, the temperature is raised to 410° F. for a short time. The first stage of the reaction is complete; the resin is a yellowish, transparent solid, soluble in acetone. Mixed with a filler and heated for several hours to the moderate temperature of 185 to 221° F., the material changes to a hard, infusible product. The reactions are:





The carboxyl marked with an asterisk may react further, permitting the molecule to grow.

TABLE 131.—*Production of plastics materials (1947).**
Condensation products.

	Pounds	Value per pound
Phenolic resins		
Phenolformaldehyde	149,393,000	$0.34
p-tert.-butylphenol-formaldehyde	4,852,000	0.36
Cresolformaldehyde		
Resorcinol-formaldehyde	917,000	—
Total unmodified resins	177,636,000	0.32
Modified by rosin ester or rosin	35,817,000	0.24
Total modified	39,247,000	0.25
Ureaformaldehyde resins	94,914,000	0.30
Melamine-formaldehyde type	17,487,000	0.53
Alkyd resins		
Phthalic alkyd resins (total)	224,120,000	0.39
Phthalic alkyd-glycerol	134,324,000	0.40
Phthalic alkyd-pentaerythritol, modified by rosin ester	12,292,000 29,145,000	0.35 0.38
Maleic anhydride-glycerol unmodified	1,150,000	0.37
Maleic alkyd-pentaerythritol-rosin ester	21,787,000	0.21
Total maleic alkyd alkyds, modified	46,717,000	0.24
Total alkyd resins	283,064,000	—

* U. S. Tariff Commission.

Nearly all the condensation products may be produced, by variations in the manufacturing process and formulation, in the form of oil-soluble resins for protective coatings; "varnish" for laminates; adhesives and cements; liquids for impregnating electric coils, thus insulating each one; and for the induration of plaster of paris (resorcinol-formaldehyde). Layers of canvas coated with resin varnish, laid one on another and hot-cured in a hydraulic

press produce a hard, strong board, water-resistant, and with superior electrical insulating properties; resin varnish-coated paper is similarly assembled and cured to form an even stronger board. To these long-established industries, there has been added a newer one: layers of wood coated with resin adhesive are cured under enormous pressure, by which the wood is compacted. There results a material (Compreg) of much higher density than the original wood, which has valuable properties, applicable to new uses and services.

Reference has been made in several places to resins suitable for protective coatings, and most of these are soluble in oils. Among the materials added to the reaction kettle in order to "modify" the resin produced (generally to make it oil-soluble) is ester gum, and kindred gums.

Ester gum is glyceryl abietate, also called glyceryl resinate, and is made by boiling melted rosin with 11 to 12 per cent of its weight of glycerin, distilling off the water formed. The product after cooling looks very much like rosin, and has a faint odor similar to that of rosin, but it is less brittle, and its acid number is 15 and less instead of 165; this means a greater resistance to water. It has all the remarkable oil-solubilities which rosin has.

Rosin is essentially abietic acid, $C_{20}H_{30}O_2$, with which glycerin forms an ester; glycerin triresinate is the preferred form,[4] but the commercial product usually contains small amounts of di- and mono-resinates.

$$\text{Rosin} + \text{glycerin} \rightarrow \text{ester gum} + \text{water}$$

Phenolformaldehyde resins dispersed in ester gum are available under several trade marks.[5] Since 1928, there has been available a 100 per cent phenolformaldehyde oil-soluble varnish resin.[6]

Glycerin and phthalic anhydride condensed in the presence of the fatty acids from linseed oil yield oil-soluble resins, such as "modified Glyptal," which have proved very satisfactory. "Oil-soluble Rezyl" is another well-known representative of this class, and contains fatty acids, or rosin, or both. "Oil-soluble Teglac" is a glycerin-phthalic anhydride condensate modified principally by rosin.

The oil-soluble alkyd resins[7] are a group of resins including among others an ethylene glycol-phthalic anhydride condensate modified by unsaturated fatty acids from a drying oil. In general the oil-soluble alkyd resins for varnish making may be said to be esters of polybasic acids and polyhydric alcohols, modified by unsaturated fatty acids such as oleic acid, or by oils of the drying type.

Thermoplastic resins are generally shaped in an injection press, a horizontal press automatically operated. The resin, properly compounded and colored, is fed into the hopper as granules, small cubes, or flat platelets, whence it drops into the heated chamber, fitted with a plunger, a spreader,

[4] *Paint Varnish Prod. Mgr.*, 8, Dec., 1932, sect. 1, p. 5.

[5] Such as Amberol, Beckacite; but it should be remembered that the trade name does not establish the exact nature of a product; under the same name, several products may be made.

[6] P. 313, "Protective and decorative coatings," vol. I, Joseph Matiello, New York, John Wiley and Sons, 1941.

[7] *Chem. Met. Eng.*, 39, 599 (1932).

TABLE 132.—*Production of rosin esters (1947).**

	Pounds	Value per pound
Rosin (abietic acid)-glycerol	39,472,000	$0.19
Tall oil esters	3,032,000	.19
All other unmodified rosin esters	28,032,000	.17
Rosin esters, grand total	78,280,000	.20

* U. S. Tariff Commission.

and the mold. The resin compound fuses, and flows under the pressure applied into the relatively cold mold, where it becomes rigid. The mold almost always has a number of cavities, all fed from one central sprue; it is called a family mold. When the mold opens, the molded article is pushed out by the discharge pins, and removed by the operator (see Figure 246).

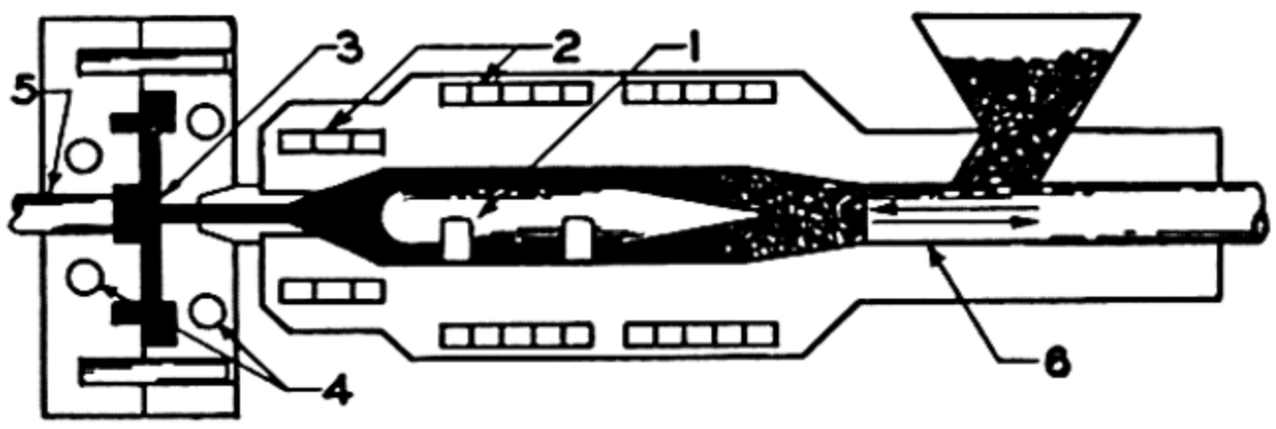


FIGURE 246.—Sketch illustrating the principle of the injection molding press: (1) spreader, (2) heaters, (3) mold, (4) cooling channels, (5) discharge pin, and (6) plunger.

Thermosetting resin compounds are molded in a compression press, generally horizontal, with a single- or multiple-cavity die. Heat is supplied, generally by steam, the steam pressure being regulated to furnish the temperature required. The steam circulates in channels provided in the die, which is made of hardened steel. The operation of the press is generally automatic. The presses vary from 50 to 500 tons total pressure.

The principle of the compression press is shown in Figure 247. Either a

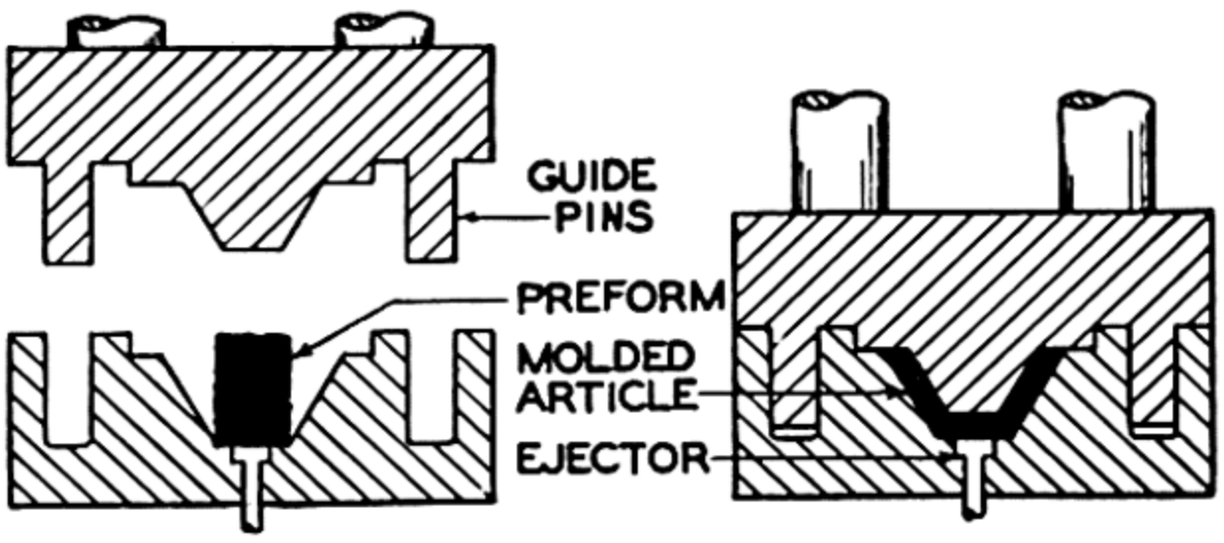


FIGURE 247.—Sketch illustrating the principle of the vertical hydraulic compression press, for molding compounds containing thermosetting resins. A single-cavity press is shown.

"preform" or a weighed quantity of granules or powder is placed in each cavity. Examples of molding, with weights, and the method employed are given in Table 133.

The transfer molding system is an adaptation of injection molding to thermosetting molding compounds. In a four-cavity press, for example, four electrically preheated preforms are placed. When the press closes, the compound, which has now softened, is forced by a plunger (through gates) into the cavities in the mold which is kept hot. The pressure applied is 2600 pounds per sq in. The pieces are heat-set; when the press opens, they are removed, still hot, and set to cool somewhat on a rack before further handling. (See Table 133 for details.)

TABLE 133.—*Examples of the molding of plastic articles.*

Piece and color	Resin	No.†	Preform or powder	Weight of total charge	Cycle (min.)	Temperature in mold (°F.)	Type of molding
Black piano key	Phenol-formaldehyde	20	preforms (20)	310 grams	1½	340	Compression
Red-brown toaster base	"	1	preforms	467 grams	1½	340	"
Black kettle handle	"	6	preheated preforms	600 grams	1.64	340	Transfer
White disinfectant dispenser	urea-formaldehyde	1	powder	453 grams	2½	300	Compression
Clear flat window for radio 12x18 cm	methyl methacrylate	1	granules (cubes)	78 grams	2	140 or less	Injection*
½" diameter balls, black**	cellulose acetate	50	granules (cubes)	102 grams	2½	"	"
Ivory dashboard knobs§	"	8	granules (cubes)	72 grams	2	"	"
Clear rectangular light dousers‡	methyl methacrylate	8	granules (cubes)	70 grams	1¾	"	"
Engraved wedding ring box	"	8	granules	72 grams	1	"	"

* The granules are heated to above their softening point, between 300 and 500° F., as required.
† The number of pieces made at each closure of the press.
‡ Made for the U. S. Army Signal Corps.
§ Material preheated 4 hours at 150° F.
** Experimental.

Products of Polymerization

Vinyl Resins. The monomer of a vinyl resin contains an ethylenic double bond. As the double bond opens, through the influence of heat, or otherwise, it furnishes two free valences; if polymerization is to take place, one of these valences is directed to a similar freed valence of a second molecule, and the other to one of the free valences of a third molecule. The resulting trimeric structure still has two available valences, with both of which further growth can take place.

The simplest ethylenic molecule is ethylene ($CH_2:CH_2$) and the simplest vinyl polymer is polyethylene or polythene, which may be expressed as $(-CH_2-CH_2-)_n$. It is made by compressing ethylene gas to 1000 atmospheres and passing it through a reaction coil held at 200° C. in its upper part, and 120° C. in its lower part. Oxygen in the quantity of 0.01 per cent is used as catalyst. The molten polymer is separated from the unreacted gas, and the latter recirculated.

Low-pressure polymerization employs benzoyl peroxide as catalyst, and a solvent. An emulsion polymerization has been proposed.[s]

Polyethylene resin reaches the molder in the form of small flat hard chips 3 mm wide and 1 or 2 mm thick, packed in the cardboard drum. Much of the resin consumed is colorless. Polyethylene resins are straight-chain polymers of ethylene, produced in a wide range of molecular weights. They yield semi-rigid, waxy, translucent plastics, with excellent electrical insulating characteristics. One of its popular forms is that of a thin, colorless film, with the slight wax-like appearance, not transparent, but translucent; such film may be extruded in the form of a tubing, and the latter made into bags by heat-sealing one end. There are numerous other forms and uses.

"Vinylite" (polymerized vinyl chloride) in blocks of some thickness is water-white and transparent to ultra-violet light. Polyvinyl acetate is an odorless, tasteless, colorless, thermoplastic resin. It is insoluble in water, fats and waxes, but is soluble in organic solvents. Polyvinyl chloride-acetate is a copolymer of the chloride and acetate, and combines the best properties of both in a single material. It is odorless, non-inflammable, tough, has excellent water resistance and good dielectric properties. Vinyledene chloride resins are polymerized vinyledene (unsymmetrical dichloroethylene). This is frequently copolymerized with vinyl chloride, the degree of copolymerization being varied to produce resins ranging from a flexible, moderately soluble material softening at 158° F., to a hard, tough, thermoplastic resin softening point at 356° F.

Dioctyl phthalate is a preferred plasticizer for the vinyl resins. Its production in 1947 was 18,000,000 pounds (45.6 cents a pound).

Methyl Methacrylate Resins. Methyl methacrylate resin plastics enjoy a special distinction, because under the names of "Plexiglas" and "Lucite" they served during World War II for making curved hoods protecting the cockpit in many types of airplanes. They are colorless, clear as glass, essentially unbreakable, strong, and difficult to set on fire. They are made into sheets, rods, and other shapes.

[s] U. S. Pat. 2,342,400. See also "Polyethylene, a new plastic makes rapid progress," *Chem. Ind.*, 60, 219 (1947).

Methyl methacrylate (the monomer) is a liquid, which is made from acetone cyanhydrin [$CH_3 \cdot C(OH)(CN) \cdot CH_3$, from acetone and hydrogen cyanide], by hydrolyzing it to $CH_3 \cdot C(OH)(COOH) \cdot CH_3$, removing the water (strong acid) to give methyl acrylic acid [$CH_2:C(CH_3) \cdot COOH$], and esterifying the latter [$CH_2:C(CH_3) \cdot COOCH_3$]. The liquid is polymerized by heat, light, sodium peroxide, or benzoyl peroxide, giving products which range from soft to hard solids, depending upon the degree of polymerization. The granulated hard solid is the resin shipped to the molder; it is already polymethyl methacrylate, and is shaped on an injection press. The clear liquid monomer, suitably inhibited, is also supplied; with a catalyst, it is poured into molds and there is allowed to polymerize and harden. The hardened sheet or casting is then baked for several days at 110° F. to complete the polymerization.[9]

Polymethyl methacrylate rods 1¼ inch in diameter are extruded hot and must be cooled gradually. The rod enters a jacketed die cooled with warm water (195° F.), then passes on to cooler sections. A high volume shrinkage takes place on cooling (12 per cent) which is constantly made good by the high pressure on the soft mass (1600 lbs./sq. in.). Rapid cooling of the rod would case-harden it and cause the formation of bubbles in the interior. The moving rod is lubricated with a high-pressure lubricant.

Polystyrene resin, as furnished to the molder, consists of small triangular pieces 3 mm wide and 3 mm high. It is colorless, clear and brilliant.[10] Polystyrene is molded mainly in its transparent, colorless state into refrigerator boxes, salt cellar tops, and many other articles; colored polystyrene ("Lustron") is made into wall tiles. Polystyrene has been made into bottles. In the form of rods and sheets, polystyrene is harder to keep shiny than polymethyl methacrylate. It has been found beneficial to anneal polystyrene rods, slabs and other articles.[11]

TABLE 134.—*Production of vinyl resins, polystyrene, and acrylate resins (1947).**

	Pounds	Value per pound
Polyvinyl chlorides and copolymers	136,136,000	$0.35
Polyvinyl acetate, butyral, formal, alcohol, ethers	41,307,000	0.57
Polystyrene resins	105,866,000	0.27
Other nonbenzenoid resins, mainly acrylates	81,650,000	1.44

* U. S. Tariff Commission.

Products of Degradation

Cellulose-derived Resins. The resins and plastics resulting from condensation and polymerization reactions consist of polymers which are built up from monomers—simple substances of low molecular weights; cellulose-derived plastics, on the other hand originate in a large molecule which is reduced in weight, hence "degraded," in the course of processing. In general,

[9] Cast polymethyl methacrylate is not thermoplastic in the true sense; it is only partly thermoplastic, and can be stretched 4 to 1, but not indefinitely.

[10] The exact designation is, for example, Dow polystyrene, formula 665 K_m, clear, number 6.

[11] "Annealing of styrene and related resins," James Bailey, *Modern Plastics* (October. 1946).

there is at the same time a chemical modification. It would not be incorrect to term the cellulosic resins and plastics "semi-synthetic."

The first cellulose plastic, which was also the first plastic in the modern sense, consisted of cellulose nitrate plasticized with linseed oil and camphor and named "Celluloid."[12] An early formula was:

	Parts by wt
Camphor or camphor oil	20
Castor or linseed oil	40
Nitrocellulose or "xylodine"	40

The method of preparation consists of mixing the water-wet nitrocellulose with powdered camphor, sprinkling alcohol on the mix, and kneading at a low temperature for several hours. At this lower temperature (35° C.) the operation is safer than at the higher temperature necessary for dryer materials. The resulting mass is soft, and by heat and pressure it is formed into sheets, blocks, and other shapes.

Pigments are incorporated during the kneading; zinc white, for example, gives a white resembling ivory. For transparent plastics, urea is added as stabilizer (antacid); in white "Celluloid," zinc oxide acts as both pigment and stabilizer.

Camphor not only plasticizes pyroxylin, (another name for nitrated cellulose) but robs it of its explosive property. The shaped articles must be allowed to season in closets at 30° C., until all solvents have evaporated.

A special kind of pyroxylin plastic is used for the manufacture of moving picture films; the camphor for this purpose is usually purified by solution in alcohol and filtration; the formula specifies a higher proportion of pyroxylin which is dissolved in methanol, amyl acetate, and other combinations of solvents, to produce at once a thick solution low in camphor (3 per cent). This solution is fed to a large cast-iron wheel (15 feet in diameter and larger), perfectly balanced, with its 18-inch face silvered and polished; the wheel turns slowly, so that the liquid fed in at one place dries sufficiently to permit removal before a whole revolution has been made. The film is continuous, and wide enough to give a number of strips of the standard size (32 mm. wide) for moving-picture cameras. The film base, after suitable drying, is coated with the gelatin carrying the silver salts.[13]

There are a number of other formulas for pyroxylin plastic films for moving pictures and cameras. In addition, cellulose acetate film, which is not inflammable, was introduced some years ago, and is now standard. The acetate film is a safety film.

"Fabrikoid" is a material which resembles leather and serves many useful purposes, such as bookbinding. It is made by coating cloth with pyroxylin made into a free-flowing jelly by the addition of suitable solvents.

"Aroclors" are chlorinated biphenyls, sold in the form of thick oils or resin-like solids, whose chief use is in lacquer formulations. "Halowax" is a

[12] The name was coined by the Hyatt Brothers; John Wesley Hyatt took out many patents, for example U. S. Patent 88,633 in 1869. In that day, the development of the new plastic was a greater sensation than that of the synthetic resins has been in the past decade. Other similar plastics are Pyralin, Viscoloid, Fiberloid. The word nitrocellulose is still in general use and means nitrated cellulose.

[13] Chapter 37.

chlorinated naphthalene produced in the form of a wax or oil. The wax is used as a condenser impregnant, in flame-, acid- and insectproofing wood and fabrics, and in flameproofing wire and cable.

In its present improved form, "Celluloid" and other pyroxylin plastics are made in transparent, colorless sheets, in a variety of brilliantly colored and mottled sheets, both transparent and opaque, and in other rigid forms.

Cellulose acetate is a popular resin for molding materials, partly because, unlike the untreated nitrate, it is not inflammable. Its manufacture is outlined in Chapter 22. The cellulose acetate flakes, with plasticizer, solvents and dyes, are mixed warm (300° F.) in a Banbury mixer; the plastic mass which forms in a short time is sheeted between rolls, cooled, and granulated into molding powder. The plasticizers used are dimethyl phthalate, diethyl phthalate, triphenyl phosphate and other phthalate esters, all high-boiling substances of low vapor pressure at room temperature. A compression molding powder may have the following composition: [14]

Cellulose acetate flakes	66.7%
Methyl phthalyl ethyl glycollate	22.2
Triphenyl phosphate	11.1

Cellulose acetate plastics are made in clear, almost colorless sheets, and in all shades of color, clear or opaque.[15]

Cellulose acetate-butyrate with not over 20 per cent plasticizer (its usual formula) is in active demand; it has a greater dimensional stability than has the acetate, and resists weather and temperature better.[16] Cellulose propionate has unique electrical resistance.[17] All cellulose-derived resins are thermoplastic.

The production of plasticizers for all kinds of resins is considerable, as indicated in Table 135.

TABLE 135.—*Production of plasticizers for synthetic resins and allied materials (1947).**

	Pounds	Value per pound
Phthalic anhydride esters	74,361,000	0.36
Tricresyl phosphate	11,939,000	0.34
Total cyclic esters	103,408,000	0.36
Acyclic plasticizers, mainly esters, including 9,063,000 pounds of stearic acid esters	44,693,000	0.43

* U. S. Tariff Commission.

Ethyl cellulose is made by the reaction of ethyl chloride on alkali cellulose (Chapter 22) in a pressure vessel, under the influence of heat:

$$\text{Cellulose}(ONa)_n + nC_2H_5Cl \rightarrow \text{Cellulose}(OC_2H_5)_n + nNaCl$$

After the reaction, the content of the ethylator is a doughy mass; it is dropped into water, where it precipitates in the form of granules and flakes. The latter are washed free of salt and dried. It is plasticized with diamyl-

[14] Simmonds, p. 43 (1941).
[15] A sample string carries 75 sample plates of different colors, each plate being cut to four thicknesses to show the relation of color to the thickness of the sheet.
[16] Example: "Tenite" II, formula 239E-18765-Hz-white.
[17] Example: "Forticel," cellulose propionate, formula 28228, color green.

naphthalene and mineral oil, for certain results (low-temperature resistance); with triphenyl phosphate, butyl "Cellosolve" stearate and dibutyl phthalate for others; with castor oil, corn or cottonseed oil for still others. The flexible form of ethyl cellulose plastic is made from molding material containing 35 to 55 per cent plasticizer; the more rigid forms are obtained with molding powders carrying 10 per cent (or so) of plasticizer.

TABLE 136.—*Shipments and consumption of cellulose-derived products (1948).**

	Pounds
Cellulose acetate and mixed ester plastics,‡	63,556,290
Nitrocellulose plastics†	10,409,412
Other cellulose plastics	8,632,800

* Office of Domestic Commerce; figures extended from 9 months' total.
† Nitrocellulose in lacquer not included.
‡ Includes fillers, plasticizers and extenders.

Casein Plastics

Still another plastic, in a class by itself, is *casein plastic*, of which "Galalith" is an example. The raw material is casein, the white curds which separate from skim milk on addition of lactic or acetic acid, or of rennet, an enzyme obtained from the calf's stomach lining. The rennet casein is higher in ash content (7 per cent) than the acid-precipitated casein, and is preferred for the manufacture of the plastic. After precipitating the casein, there is left, in the milk liquor, milk sugar and albumen, which may be recovered. Much of the casein is imported, in the form of dry granules.

In order to prepare the plastic, the casein is powdered, mixed with a coloring matter or a filler, moistened with enough hot water to form a dough, which is then passed between heated rolls to form sheets. A number of sheets may be pressed to a block or other shape, while rods and tubes are made directly by means of an extrusion machine. The shaped pieces are placed in a solution of formaldehyde, which "sets" them, that is, renders them as hard as stone; finally they are dried in a warm closet.

The most important outlet for these hardened sheets is for the button trade. Very beautiful results may be produced by incorporating a pigment in the original mass, shaping the button, dyeing it on the surface, cutting a design which exposes the body color, contrasting with the surface color.

Casein is used for many other purposes, for example as a glue and for sizing paper.

Miscellaneous Plastics

Among the many newer resins may be mentioned polytetrafluoroethylene ("Teflon"), a solid polymer which resists heat, alkalies, strong mineral acids, or organic solvents.

Nearly as heat and chemical resistant as "Teflon" is "Kel-F,"[17a] the polymer of monochloro trifluoroethylene; it is thermoplastic. It is supplied in several grades of hardness from flexible to highly rigid.

The numerous organic silicon products (collectively called "silicone" resins) are used for bonding mica, glass fibers and asbestos for electrical

[17a] Developed during the war, now obtainable from M. W. Kellogg Co., P. O. Box 469, Jersey City 3, N. J.

insulation. These new thermosetting resins, once set, resist high temperatures and moisture. They are prepared from silicon organic chloride, such as $(C_2H_5)_2SiCl_2$ (diethyl silicon chloride), which may be hydrolyzed to give ethyl silanediol. The latter may produce a polymer by condensation, eliminating water. Hydrolysis and condensation of various substituted

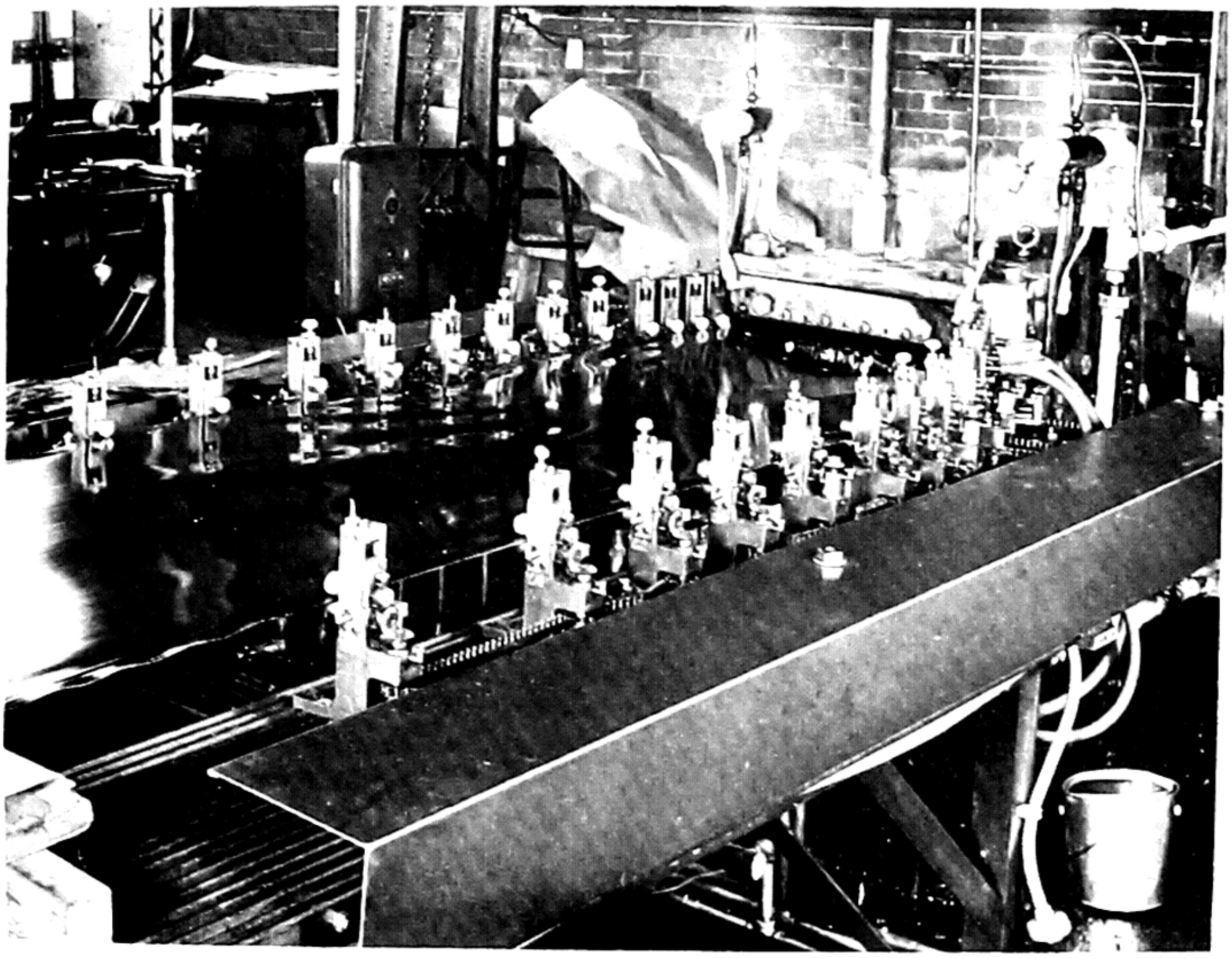


FIGURE 248.—Extrusion and sheet-forming machine for plastics. The sheet is extruded at right, and moves toward the left. It consists of cellulose acetate butyrate, Tenite II, ivory color. Note the small pulleys set gradually further back, so that the sheet is held, guided, and furthermore stretched sidewise, while it is stretched lengthwise by the rollers. (Courtesy of The Plax Corporation, Hartford, Conn.)

chlorosilanes may give rise to an infinite variety of polymeric products varying from liquids to hard, glass-like solids.

Resins made by the condensation of furfuryl alcohol with itself are in process of development.

Working and Forming Plastics.

Sheet plastics may be extruded through a longitudinal opening in a die. The material may be, for example, a pigmented cellulose acetate ("Tenite" I). As the sheet emerges it meets small rollers set at its edges, and set gradually farther back, so that the sheet is stretched sidewise. The sheet cools very gradually as it moves (on rollers) over the relatively short distance

to a punch press, which cuts it into suitable lengths and shapes. The sheet produced is highly lustrous as well as strong.

Polystyrene sheets as first produced are brittle and weak. By extruding to the forming machine with numerous small pulleys at the sides set gradually farther back, and by winding the sheet on a driven roll, a clear, transparent, colorless sheet is formed ("Polyflex"), which is flexible and several times stronger than polystyrene.[18]

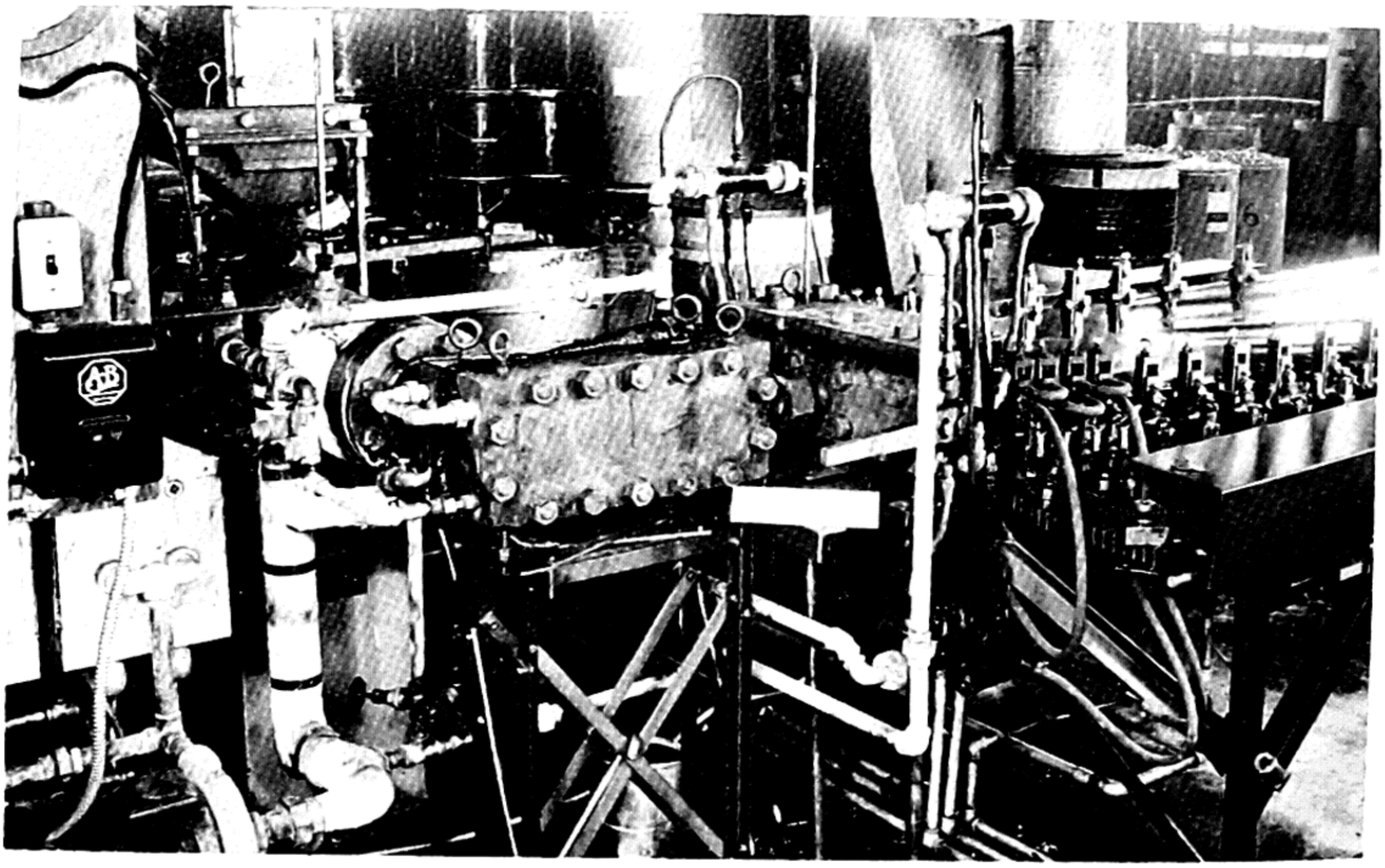


FIGURE 249.—Another view of the extrusion and sheet-forming machine, taken from the pressure end. (Courtesy of The Flax Corporation, Hartford, Conn.)

Plastic bottles[19] for special purposes are produced on automatic blowing machines: for example, a polyethylene bottle with flexible walls (6-ounce), light brown in color (for spraying perfume by compressing the bottle); a clear bottle of rigid polystyrene; and others. The polyethylene bottle is made by extruding a tubular section of the hot plastic, pinching one end closed, and blowing it out (4 lb air pressure) against the walls of the mold. The discharged bottle is cooled by a water spray. Plastic bottles have the great advantage of being unbreakable; the cost is, however, too high to permit their extensive use; they would cost about 4 times as much as glass bottles. Cellulose acetate bottles have been produced and tried in practice; it was found that their walls were not water vapor-tight. A playing ball of cellulose acetate has been produced on the blowing machine.

[18] "Stretch orientation of styrene and its interesting results," James Bailey, *India Rubber World* (May, 1948). U. S. Pat. 2,297,645, 2,412,187, 2,365,374.

[19] "Blow molding of thermoplastics," James Bailey, *Modern Plastics* (April, 1945). U. S. Pat. 2,349,176.

Synthetic Phenol

The rise in the production of phenol resins of various kinds made it imperative that new sources of phenol be found. Natural phenol is obtained from coal-tar. Synthetic phenol is made from benzene, by one of three methods: sulfonation followed by alkaline fusion, or by chlorination and subsequent heating under pressure with caustic soda solution, or by the vapor phase regenerative process.[20] The war emergency has made it necessary that military needs for phenol be filled first; it is indeed a fortunate circumstance that these several methods for obtaining phenol had been developed and well established. There were produced in 1947, 22,147,000 pounds of natural phenol, and 243,122,000 pounds of synthetic phenol, with unit value of 11 cents and 10 cents, respectively.

Benzene Sulfonate Method. In the early developments, benzene C_6H_6 was treated with oleum, the benzene sulfonate $C_6H_5 \cdot SO_3H$ was isolated by neutralizing both excess acid and sulfonate with lime, and filtering the calcium sulfate from the solution of calcium benzene sulfonate. An improvement was made when the continuous sulfonation method of Dennis and Bull was installed.[21] Four sulfonating tanks are used in series, and in each, the benzene enters at the base through perforated pipes, so that it rises in the form of fine droplets. The sulfonated benzene remains dissolved in the great excess of benzene which is provided. The benzene flows countercurrent to the acid; the latter is 98 per cent H_2SO_4 at the entry to the first tank, 77 per cent at the exit of the fourth, when its sulfonating power is exhausted. It is concentrated to 93 per cent and new oleum is added to it, to reach the required 98 per cent strength. The benzene with 2 per cent sulfonate is washed with water (3 washers), the sulfonate in the water solution neutralized with sodium sulfite recovered from the last step in the process, and concentrated.

$$2C_6H_5 \cdot SO_3H + Na_2SO_3 \rightarrow 2C_6H_5 \cdot SO_3Na + SO_2 + H_2O.$$

The strong solution of sodium benzene sulfonate is run, gradually, into fused caustic soda at 320° to 350° C. (608° to 662° F.); sodium phenolate and sodium sulfite are formed.

$$C_6H_5 \cdot SO_3Na + 2NaOH \rightarrow C_6H_5 \cdot ONa + Na_2SO_3 + H_2O.$$

The melt is dissolved in a limited amount of water, sufficient to dissolve the sodium phenolate only; the sodium sulfite remains as a wet solid, which after washing and drying, serves for the neutralization of new amounts of benzene sulfonate. Only half the sulfite produced is needed in this way; the other half may be sold (by-product).

The sodium phenolate in solution is decomposed by carbon dioxide from a lime kiln; phenol and sodium carbonate are formed.

$$2C_6H_5 \cdot ONa + H_2O + CO_2 \rightarrow 2C_6H_5 \cdot OH + Na_2CO_3.$$

The latter is causticized by lime from the kiln. To complete the reaction,

[20] "Phenol, Part I," R. F. Messing and W. V. Keary, *Chem. Ind.*, 63, 43 (1948), and "Part II," with three flowsheets, on p. 234.

[21] *Ind. Eng. Chem.*, 10, 738 (1918).

a small amount of nitre cake is added. The phenol separates as an upper layer; it is run off and distilled from a pot still.

Chlorbenzene Method. For many years attempts were made to produce phenol commercially from chlorbenzene, without result. It remained for an American firm to discover the proper apparatus, reaction mix and operating conditions which have made the process a commercial success. Starting with chlorbenzene, the method as practiced is as follows: [22, 23]

Chlorbenzene (1 mole) is emulsified with a 10 per cent aqueous caustic soda solution (1¼ mole) and the emulsion (oil droplets in water) pumped under a pressure of 200 atmospheres into a multitubular reaction vessel, with recirculation, and continuous discharge of a small portion which is just made up by the entering emulsion. The liquid travels through the tubes with a sufficient turbulence to maintain the dispersion of the chlorbenzene. The tubes are made of copper, in several units 1¼ inch outside diameter, with thick walls; a temperature of 320° C. (608° F.) is maintained by means of diphenyl oxide vapor under moderate pressure. The copper wall acts as a catalyst. As the phenolate forms, it dissolves in the water. The conversion is nearly 100%, if the circulation period allows any one part of the charge to remain within the tubular vessel for 50 minutes. The reaction is:

$$C_6H_5Cl + 2NaOH \rightarrow C_6H_5ONa + NaCl$$

chloro-benzene

On leaving the reaction vessel, the liquid passes through the exchanger to heat the incoming liquids, then through coolers, after which the pressure is released. The free phenol is formed by a treatment with acid, giving two layers.

$$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$$

phenol

The upper layer is run off and distilled from a chromium-plated still,[24] some water passes over first, next any unchanged chlorbenzene, near 132° C. (270° F.), then the phenol, near 181° C. (358° F.), while diphenyl oxide remains in the still. The latter's boiling point is 259° C. (498° F.). The recovery of phenol is nearly the theoretical one.

Raschig Method. The Raschig method for making phenol, also called the "vapor phase regenerative process," is producing at a rate exceeding[25] one million pounds of phenol a year (in one plant alone).[25] The process is in two stages. In the first one, monochlorbenzene is produced by the action of a catalyst from benzene, hydrochloric acid and air, in a first converter.

$$C_6H_6 + HCl + \tfrac{1}{2}O_2 \rightarrow C_6H_5Cl + H_2O.$$

In a second converter, the chlorbenzene is hydrolyzed catalytically with steam, producing phenol and regenerating the hydrochloric acid for further use.

$$C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl.$$

[22] *Ind. Eng. Chem.*, 20, 114 (1928).
[23] U. S. Patent 1,607,618.
[24] U. S. Patent 1,824,867.
[25] "Phenol made by vapor phase regenerative process," by Theodore R. Olive, *Chem. Met. Eng.*, November, 1940, with a pictorial flowsheet, p. 789-792.

Still another method has been described briefly in a letter.[26]

An attempt has been made to hydrolyze benzene sulfonic acid with aqueous caustic,[27] under pressure and at elevated temperature, as in the chlorbenzene method.

It has been proposed to make phenol from benzene by sulfur trioxide action in liquid sulfur dioxide.[28]

Uses. The main consumption for phenol in peace time is the synthetic resin industry. A sizable quantity serves as disinfectant and preservative, while about 4 million pounds a year are the starting material for the manufacture of pharmaceuticals, such as salicylic acid and derivatives, and dye intermediates. In war time, phenol serves for making certain explosives.

Formaldehyde

Formaldehyde, CHOH, is a gas which dissolves in water to form a concentrated solution; it is this solution which enters the market. Formaldehyde is made by the partial oxidation of methyl alcohol catalyzed by copper gauze, or other agents. A mixture of air and alcohol is provided by bubbling air through warm methyl alcohol in a copper vessel fitted with steam coils. The air-alcohol mixture passes a dephlegmator held at 40° to 50° C. (104° to 122° F.) and then enters the oxidizer. The oxidizer is a cast iron vessel with a central flue which facilitates the elimination of the heat of reaction. The gaseous mixture passes across a layer of copper filings which acts as catalyst, and which maintains itself at 550° to 600° C. (1022° to 1112° F.) by the heat liberated during the reaction. The gases leaving the converter contain formaldehyde, some methyl alcohol, nitrogen and water. They must be cooled suddenly in order to prevent side reactions; this is accomplished by passing them at once to an absorber, where a cool hydrous solution meets them, and at the same time abstracts the formaldehyde. There is formed a water solution containing 30, 35, or 40 per cent CHOH by weight, and some methyl alcohol, esters and methylal. In a second absorption vessel, methyl alcohol is retained. The outgoing gases are scrubbed for small amounts of alcohol, the weak solution concentrated in a column still, and the recovered material used in the process. The crude formaldehyde may be refined by a distillation.

Operating as just described, the yield lay between 60 and 65 per cent. It was found that by maintaining the reaction mixture neutral, the formation of by-products is decreased, and the yield correspondingly raised. The neutrality is insured by feeding a small amount of ammonia to the entering gas mixture.[29]

The explanation of the reaction is that, first, the methyl alcohol molecule is dehydrogenated by the metal. Next, oxide formation by the metal takes place, and this is the function of the air. The oxide reacts with the hydro-

[26] "Synthetic phenols for resin manufacture," by Henry Howard, *Ind. Eng. Chem.*, 33, 1581 (1941).

[27] U. S. Patent 1,789,071.

[28] U. S. Patent 2,007,327.

[29] U. S. Patent 1,738,745, quoted through Marek and Hahn, "The catalytic oxidation of organic compounds in the vapor phase," New York, Chemical Catalog Co., Inc., 1932, p. 148.

gen, removing it from the system, thus allowing the dehydrogenation to proceed further. The water formed leaves with the formaldehyde. The net reaction is

$$2CH_3OH + O_2 \rightarrow 2CHOH + 2H_2O.$$

To copper, and other metallic catalysts, two substances are poisons in the formaldehyde reaction; they are acetone and water. For this reason synthetic methanol, furnished free of acetone as well as anhydrous, is to be preferred to wood alcohol. With vanadium pentoxide as the catalyst, however, methyl alcohol with as high as 5 per cent acetone may be used, without loss of efficiency. The temperature, moreover, is only 225° C. (437° F.)[30]; in all cases, the lower the temperature, the higher the yield.

A catalyst consisting of iron and molybdenum oxide has been found to be very effective; the molybdenum possesses directive power, while the iron has a high activity for conversion. A lower temperature is sufficient.

The partial hydrogenation of carbon monoxide to formaldehyde has not succeeded commercially,[31] in part probably because the reaction

$$CO + H_2 \rightarrow CHOH - 0.7 \text{ Cal.},$$

is slightly endothermic, while

$$CHOH + H_2 \rightarrow CH_3OH + 27.9 \text{ Cal.}$$

is strongly exothermic.

In one process, the direct, limited oxidation of natural gas with the recovery of formaldehyde has progressed well. A typical oxygenated crude liquor contains 35 per cent methanol, 20 per cent formaldehyde, 5 per cent acetaldehyde as principal products.[32] The contribution to the production of formaldehyde from this source is increasing every year.[33] In another process, natural gas is oxidized at 20 atmospheres pressure and about 450° C. with a limited volume of air, in the presence of a copper-containing catalyst. The products are methanol, formaldehyde and acetaldehyde. The formaldehyde is isolated by distillation.

Formaldehyde is extremely reactive; its uses are correspondingly numerous. It serves as an insecticide and disinfectant (Chapter 38), as a chemical reagent in synthesizing organic compounds, as an embalming fluid, as a hardening agent for casein; its most important use from the standpoint of tonnage is for the manufacture of synthetic resins.

In 1947, there were produced in the United States 615,853,000 pounds of formaldehyde (37 per cent CHOH by weight), with a unit value of $0.04; in 1948, the production was 623,837,887 pounds. In 1940, it was under 200,000,000 pounds.

Camphor. Natural camphor is obtained from the camphor tree, *Laurus camphora*, which grows in Japan and in Formosa. The tree, preferably 50 years old, is chopped small, and boiled with water at a slow rate; the

[30] U. S. Patent 1,383,059.
[31] U. S. Patent 1,824,896.
[32] *Pet. Ref.*, 25, 609 (1946).
[33] "Organics from natural gas," J. V. Hightower, *Chem. Eng.*, Jan. 1949, p. 92; with flowsheet on p. 132.

escaping steam carries the camphor away to the condenser, where the camphor forms a crust on the condensed water. The crude material obtained is pressed free of the greater part of the camphor oils, and purified further by sublimation.

Synthetic camphor, $C_{10}H_{16}O$, a white solid, is manufactured in the United States at a rate exceeding 5 million pounds a year. The raw material is pinene, itself obtained from turpentine.

Other raw materials for synthetic resins will be found under the proper heading, or by consulting the index.

Other Patents

U. S. Patent 1,946,040, catalyst for the nuclear chlorination of benzene compounds and using same; 2,068,926, method of making artificial lumber by incorporating synthetic resin forming ingredients, such as urea and formaldehyde; 2,069,183, on a Halowax; 2,069,178, method of dispersing resins and composition produced thereby; 1,793,310-2, on making synthetic resins; 1,820,816, a cheap resin from phenol and glucose; 1,753,030, a cheap resin from starch; 1,619,692, glyptal in mica composition, for commutators; 1,619,758, glyptal with mica flakes, similarly, 1,589,094; 1,806,798, process for making phenolic compounds in circulatory tubular systems; 1,851,754, manufacture of formaldehyde by passing methanol and air in contact with vanadium oxide and a combustion retarder; 1,744,295, formaldehyde from methanol; British Patent 344,796, iron carbonyls removed from the methanol insures longer life to the silver gauze catalyst. For phenol-furfural condensation products: 1,705,493; 1,398,146; 1,592,773; 1,705,495; 1,705,494; U. S. Patents 2,008,719 and 2,014,923, on polymerizing acrylic acid and esters. Can. Pat. 438,665, on drawing biaxially oriented sheet of solvent-free organic polymer; Can. Pat. 438,937, on laminated plastic light-polarizing sheets; U. S. Pat. 2,412,504, removing inhibitor from monomers, to George Goldfinger.

Problems

1. Taking the procedure for phenolformaldehyde resin by the wet method as given in the text, what will be the weight of the produced fusible resin, if the yield is 88 per cent, and nothing is lost except the water of reaction and of solution in the formaldehyde? 1000 lbs. of phenol are taken.

2. A shipment of 2500 lbs. of ester gum is made. If the ester is pure, and all glycerin triresinate, how much glycerin and how much rosin were required? The glycerin is 98 per cent, and the rosin 95 per cent abietic acid.

3. It is required to make 1000 pounds of phenol from chlorbenzene. Let the conversion be 100 per cent, how much chlorbenzene is needed? In the manufacture of chlorobenzene, the chlorination of benzene leads to a 90 per cent recovery; how much chlorine in pounds and benzene in gallons are called for? The density of benzene is 0.879. In the recovery of the hydrochloric acid, it is found that only 90 per cent of the amount evolved is absorbed, the rest is lost; how many pounds of 22° Bé. acid will be collected? Answers: 125.7 gallons benzene; 885.6 lbs. 22° Bé. acid.

4. To make 1000 gallons of formaldehyde solution of 40 per cent CHOH content with density 1.128, from methanol by air oxidation, how much methanol, in gallons, is necessary, if the yield is 60 per cent? The methanol is made by the synthesis of CO and H_2, which gives a recovery of 100 per cent; what weight of CO and of H_2 is required to make the required amount of methanol? Answers: 5833 lbs. CO, 833.3 lbs. H_2. To make the same 1000 gallons of formaldehyde directly from carbon monoxide and hydrogen, what weight of hydrogen and of carbon monoxide would be needed if the recovery is (a) 60 per cent; (b) 80 per cent?

Reading References

"Modern Plastics Encyclopedia," Plastics Catalogue Corp., 122 E. 42 St., New York 17 (annual).

"Fundamentals of plastics," Henry M. Richardson and J. Watson Wilson, New York, McGraw-Hill Book Co., 1946.

"Plastics, theory and practice," C. C. Winding and R. L. Hasche, New York, McGraw-Hill Book Co., 1947.

"German plastics practice," John M. DeBell, William C. Goggin, Walter E. Gloor, Springfield, Mass., DeBell and Richardson, 1946.

"Systematic procedure for identification of synthetic resins and plastics," T. P. Gladstone Shaw, *Ind. Eng. Chem., (Anal. Ed.)*, **16**, 541 (1944).

"Plastics, resins, and rubbers," a revised chart, showing raw materials, intermediates and final products, with formulas, Paul O. Powers, *Chem. Eng. News*, **24**, 2784-8 (1946).

"Identification of acrylate and methacrylate," M. Martin Maglio, *The Chemist Analyst*, **37**, 4 (1948) (Phillipsburg, N. J.).

"Casein and its industrial applications," 2nd edition, Edwin Sutermeister and F. L. Browne, New York, Reinhold Publishing Corp., 1939. (3rd ed. in preparation.)

"Modern views on polymerization," L. A. Jordan, J. O. Cutter, *J. Soc. Chem. Ind.*, **54**, 89T (1935).

"Plasticity, the servant of industry," Herbert Freundlich, *J. Soc. Chem. Ind.*, **53**, 218T (1934).

"The use of synthetic resins to produce a wool-like finish on spun rayon fabrics," Philip LeBrun, *Textile World*, **87**, 944 (1937).

"Recent developments in paint, varnish and lacquer technology," A. O. Plambeck, *J. Soc. Chem. Ind.*, in *Chemistry and Industry*, **53**, 692 (1934), with a list of the modern synthetic resins which are of interest to the varnish makers, by the technical designation.

"Design of a urea resin plant," A. Brothman and A. P. Weber, *Chem. Met. Eng.*, **48**, December, p. 73 (1941).

"Progress in high polymer plastics," a collection of 6 papers, *Ind. Eng. Chem.*, **34**, 449-479 (1942).

"Working transparent plastics," John Sasso, *Aviation Magazine*, May, 1942, pages 86-95, Part I.

"Injection molding," Maurice L. Macht, Walter E. Rahm, and Harold W. Paine, *Ind. Eng. Chem.*, **33**, 563 (1941).

"Manufacture of formaldehyde," Y. Mayer, *Rev. Chimie et Industrie*, **46**, pp. 34-40, 70-77, 110-116, 136-140 (1937).

"Chemistry of Commercial Plastics," R. L. Wakeman, New York, Reinhold Pub. Corp., 1947.

"Advances in plastics in the United States and in Germany," W. C. Goggin, *Chem. Eng. News*, **24**, 339 (1946).

"New forming technique," H. F. Pearson, *Modern Plastics*, **22**, 122 (Jan., 1945).

"Fire hazards of the plastics industry," Research report No. 1, The National Board of Fire Underwriters, 85 John St., New York, 1946.

"Formaldehyde," by J. F. Walker, New York, Reinhold Pub. Corp., 1945.

"Injection Molding of Plastics," Islyn Thomas, New York, Reinhold Pub. Corp., 1947.

The history of tanning reaches almost as far back as the history of man; compared with it, the science of chemistry is indeed young. Yet in the past fifty years, chemistry has furnished the tanner a new method—chrome tanning. In the older vegetable tanning, chemistry has simplified the process, furnished a partial explanation of the reactions, a wider variety of tanning agents, and methods for testing them and for controlling steps in the manufacture. With the aid of the chemical engineer, the time required for the vegetable tanning process has been shortened. It will surprise and please many readers to learn that the leather industry was seventh in order of critical industries during World War II.

Chapter 36

Leather,* Gelatin, and Glue

Leather Manufacture

Leather is the hide [1] or skin of animals, cleaned, and treated with oils, fats, vegetable tannins, chrome salts, zirconium salts, formaldehyde or one of several other so-called "tanning agents." Such treatment arrests the decay of the skin and makes it more or less pliable. Before tanning, a skin can be almost entirely dissolved in hot water, forming a solution of gelatin, whereas after tanning, the skin is insoluble. If tannin is added to the gelatin solution, the gelatin is precipitated. Glue is gelatin which has been heated longer in the water; it jells less readily, but is more sticky.

The hides of bulls, cows, oxen and skins [2] of heifers and calves are commonly used for the larger sizes; the last three give the more uniform and denser leather. The skins of sheep and goats, to a lesser extent those of the kangaroo and certain species of seals, are used for the smaller sizes; they yield softer leathers. The hide of the horse is made into leather, but is of small importance. An appreciable amount of pigskin is also tanned.

With unimportant exceptions, hides may be said to be by-products of the meat industry. The animal is raised, and later killed for its meat, and incidentally, its hide is saved and sold to the tanner. If hides were a primary product, leather would be much more costly. This circumstance carries with it also certain penalties, in that the rancher, for instance, damages the best part of the hides by branding, is less careful about insects which perforate the hide, and is at times careless in the removal (flaying) of the hide and in its curing.

The hide has an upper thin layer, the epidermis, which carries in a small depression the hair follicle and the hair itself. Below this is the derma, or corium, many times thicker than the epidermis; it is the true leather-forming substance. Making leather involves removing the hair and the epidermis,

* In collaboration with Mr. Ralph H. Wilson, Cataract Chemical Company, Buffalo, New York. In addition, the chapter benefitted by review by Dr. Edwin R. Theis, Director, Division of Leather Technology, The Institute of Research, Lehigh University, Bethlehem, Pennsylvania.

[1] The outer covering of a large animal; among cattle hides, one weighing more than 30 lbs. in the dry salted state.

[2] The outer covering of a small animal.

cleaning the flesh side from the under skin, and treating the corium so that it will no longer be susceptible to bacterial decay. The corium has a fibrous structure; untreated it will absorb water as gelatin does; in fact, it is at least 85 per cent collagen, on a dry basis, and collagen with water forms gelatin. The tanning power renders the corium fibers water-resisting, within limits. Hides are not uniform in thickness throughout their area; the thickest part is at the butt.

The skins of the seal, walrus, and the porpoise have been made into leather for many years; within the last 25 years, the skin of the shark and the ray have been utilized. The shark carries a calcareous coating over the skin, known as shagreen; this is removed,[3] from this point on the tanning is similar to that of cow hide.

Most leather is either vegetable-tanned or chrome-tanned. Chrome tanning is more modern and requires less time; it is used for the smaller skins, the "kips" and "skins" [2] of the tanner, which are made into shoe uppers. Vegetable tanning is used for sole leather and leather belting, also for the smaller skins to a certain extent. Although chrome tanning is more rapid, considerable progress has been made in the rate of vegetable tanning. Good sole leather, in some instances, is now tanned for only thirty-five days, whereas 180 days were consumed in this process fifty years ago. Chrome tanning is also used to some extent in the production of belting and sole leather.

Preliminary Treatment of the Hides or Skins. The hides are received in the hide house in various conditions. In the largest packing houses, great care is exercised in salting (curing) them. These hides are known as big-packer hides. Hides from South America, corresponding to our big-packer hides, are called frigorifico hides. Such hides are very well cured.[4] In the smaller packing houses, and abbatoirs less precaution is taken. Hides from many foreign countries are preserved merely by drying, and are known as dry hides or flint hides. At the tannery, the bundles of hides are opened; each hide examined for defects, and the ends which would not make leather, such as ears and hoofs, are cut off and sent to the gelatin or glue maker. They are then subjected to washing under a stream of water in a large revolving drum. Soaking in water restores the fibers to their normal sizes and shapes. Dried hides require a longer soaking period. Fleshing, by which operation the areolar tissues from the flesh side of the hides are removed, follows the washing and soaking operations.

Liming is next; it is done in pits flush with the floor. Hides require 4 to 7 days to pass the pits, of which there are usually three; while in the pit, the hides are occasionally handled. The effect of liming is (*a*) to loosen the hair and epidermis; (*b*) to swell the corium, which results from a division of the coarser fibers into its constituent fibrils; (*c*) to emulsify or saponify the grease normally present in the corium. This effect is due partly to the alkalinity maintained by the excess of lime, partly to its hydrolytic action,

[3] U. S. Pat. 1,338,531.

[4] Such dried hide or rawhide is durable; for instance the tabernacle of the Latter-day Saints at Salt Lake City was constructed with rawhide strips instead of nails in 1850 and is still in daily use.

and partly to bacterial action. The liming for the kips and skins requires less time, 1 to 3 days. Sodium sulfide (Na_2S) is sometimes added to the lime suspension, as it acts much faster; or sodium sulfide mixed with lime and water to a thin paste is painted on the hair side of the skins, which are then folded together, and piled on the floor over night; the next morning, the hair is loose. For certain sheep hides bearing valuable wool, the paste is painted on the flesh side; the skins are folded flesh sides together, and left piled over night; the next day the wool can be pulled out as if it merely lay there.

The hide or skin is then ready to be scraped (beam-house work), formerly by hand, over a beam; now in a machine with spiral knives rotating fast against the skin, which is moved in slowly. On the hair side the hair and epidermis are removed; on the flesh side any adhering particles of flesh and underskin. The hides are cut into butt, shoulder and belly pieces, or merely in two; they are not cut if the leather is to make belting for machinery, for which as large a surface as possible is desired. The skins are next delimed and bated.

Vegetable Tanning, Sole Leather and Belting. After deliming and washing, the hides are ready for tanning. They are suspended in nearly spent tanning liquor of the rocker yard where they are moved up and down a short distance by a mechanical rocker. The hides receive a change of liquor each day from the next stronger vat in the system until they are ready for the stronger liquors of the layer yard. In a few instances, tanning drums have replaced the rocker vats.

Contrary to the procedure observed in the rocker yard, the packs of leather are hauled out and suspended in the next layer vat in succession. When removed from the layer section or "layaways," the leather is sufficiently well tanned to make good belting leather. For such purposes it is scoured and stuffed with grease.

Sole leather, however, is given additional treatment by drumming in a concentrated tannin extract, after which it may be placed in a tempering vat where the yield of leather is still further increased. In order to improve its appearance and properties further, it is bleached and wrung, and placed in a large revolving wheel, called an oil wheel, where it receives oils, fillers and other materials. Sole leather receives 3 per cent oil; belting leather receives 10 to 18 per cent of grease, and harness leather 20 to 36 per cent. In some instances, sole leather is dry-dipped, a practice which means immersing the dry leather in a strong solution of tannin. In such instances, the leather is given half of the materials usually added in the oil wheel, dry-dipped, bleached, and treated with the remainder of the oil wheel load.

The tanning materials vary in tannin content from 3 per cent in chestnut wood to 30 per cent in dried myrobalam fruit. The earliest tanning agents were hemlock bark or oak bark. As the forest receded, the tanners moved from the modest original settlement on Manhattan Island in two general directions; those using oak bark moved into Pennsylvania, Virginia, West Virginia, North Carolina and Tennessee; those using hemlock bark moved to lower New York State, Pennsylvania, Michigan and Northern Wisconsin. Several manufacturers now specialize in the preparation of concentrated

tannin extracts. Consequently it is no longer necessary that the tannery be located in the immediate vicinity of tannin supply.

As oak and hemlock became less plentiful, other sources of tannin became important. The quebracho tree of South America now furnishes more tannin to the leather world than any other form of plant life. The wood of the quebracho tree contains 20 per cent tannin; the extract contains 60 per cent (a solid). The most important domestic source of tannin in the United States is the wood of the American Chestnut tree. The liquid extract contains 25 per cent, the solid 65 per cent tannin. Unfortunately, however, the chestnut tree is being rapidly exterminated by a fungus called Chestnut Blight. Much of our present supply of this tannin is from dead wood. The bark of the mangrove tree of Borneo is an important source of tannin. Mangrove bark (cutch) extract contains 55 per cent tannin. Today the great bulk of American vegetable-tanned leather is tanned with quebracho, chestnut and mangrove tannin. Other tannins, listed in order of importance are: myrobalam dried fruit from India; wattle (Mimosa) bark from Australia and South Africa; valonia, the acorn of the oak tree of Asia Minor; gambier, obtained from the leaves and twigs of a climbing shrub in the Dutch East Indies, supplied in cubes or blocks containing 50 to 65 per cent and 35 to 40 per cent tannin respectively; and sumac from Sicily. Recently tara from Peru has been investigated; the pods contain 50 to 60 per cent tannin. It is now available for tannery use.

Chestnut is high in fermentable sugar. Because of their high fermentable sugar content, myrobalam, valonia and divi-divi are used principally as acid producers. Sumac and tara are mild tanning agents. Controlling fermentation is an old problem which has been simplified in some instances by the employment of less fermentable tanning materials. When additional acid is required, it is an easy matter to add the necessary amount of lactic or acetic acid. Serious consideration is being given to the use of sterile tannin liquors which would simplify the regulation of acidity in the tanning process. The tannins of this paragraph are pyrogallol (1,2,3-trihydroxybenzene) tannins, which on heating give the parent substance pyrogallol; with iron salts they are blue-black.

Quebracho, mangrove, wattle, gambier and hemlock belong to the catechol class; on heating them, the parent substance catechol (1,2-dihydroxybenzene) is obtained; with iron salts they give a green-black coloration. Oak bark contains both types, but principally catechol. Spruce extract, obtained by purifying the waste liquor from pulping by the sulfite process, is used to supplement the vegetable tannins in the tempering vat and dry dip. It is also used in the filling operations in the oil wheel.

In addition to the natural tannins, synthetic tanning materials are widely used. Although not in any way related to natural tanning agents, they do possess tanning properties in that after application to hide substance they cannot be washed out; the hide substance is protected against putrefaction; and the yield is increased.

There are agents which penetrate hide substance and become fixed, but on washing, the original hide qualities and weight return; such agents are best

named "pseudotanning" agents. Examples are fatty acids in organic solvents and aluminum salts. On aging, however, a limited degree of tannage is obtained with aluminum sulfate; subsequent treatment with formaldehyde or syntans increases the stability of aluminum tannages.

Edmund Stiasny patented the first synthetic tanning substances, which were manufactured under the name of "Neradols." His patents comprise water-soluble formaldehyde condensation products of phenol or cresolsulfonic acids and also condensation products of phenol or cresol, with subsequent sulfonation to obtain water solubility. Syntans have since been formulated which do not depend solely on sulfonic acid groups for solubility or tanning property, but which derive these properties also from an accumulation of weakly acid groups such as hydroxy, carboxyl, chlorine, or nitro groups. Such products closely approach the tanning properties of the natural tanning agents. Syntans are also produced by dispersing phenolformaldehyde resins in spruce extract. Syntans are used for pretanning, supplementing the natural tannins, and in bleaching operations. Several new syntans are capable of producing a fair yield of leather without the use of any vegetable tannins.

Chrome Tanning. Chrome tanning is applied chiefly to the smaller kips and skins; on leaving the deliming bath they are bated, in order to reduce the plumping which liming has caused and to render the grain smoother. This is done in a bath containing ammonium salts and small amounts of pancreatin (mainly trypsin). The effect of the ammonium salts is to reduce the pH of the skins and hence their swelling. The addition of the ammonium salts is regulated so that the skins are brought to the optimum pH range (7 to 9) of tryptic digestion, and the removal of accessory hide proteins is thereby facilitated. Smoother grain and better "feel" of the final leather result. The progress of the bating is judged by the feel of the skins; skill is required to stop it at the proper time. Next the skins are pickled in a bath of dilute sulfuric acid which penetrates the structure and prepares for the chrome salt action; common salt is added to this bath to overcome the swelling action of the acid. The skins are folded together and a number of them pressed free from water; as they leave the hydraulic press, they appear dry.

In chrome tanning a salt of chromium takes the place of the vegetable tannins. A distinction is made between the one-bath and the two-bath process. In the former the skins are placed in a drum with a solution of basic chrome sulfate; the drum is rotated for 5 or 6 hours. When penetration is complete, a solution of sodium carbonate or bicarbonate is carefully added at intervals, the drumming is continued for an hour or more, and the leather is allowed to stand overnight. The tanner usually considers chrome leather to be tanned when a sample strip does not curl or lose area when subjected to the influence of boiling water. Many good upper leathers, however, are considered to be properly tanned when they withstand a set standard of temperature, which may be appreciably below 212° F. If the leather does not stand the test well, more alkali is added and the drumming is continued. When satisfactory, the leather is hauled out and wrung.

In the two-bath process the skins are drummed or paddled in a solution of sodium bichromate and sulfuric acid; the resulting chromic acid penetrates them. However, if the skins have not been thoroughly delimed, more than one addition of acid may be necessary. The chromic acid-impregnated skins are later treated in a solution of hypo and sulfuric acid; the resulting sulfurous acid reduces the chromic acid to the basic compound, in which state it combines with the skins and tans them. Upon completion of the drumming, if the pH of the chrome liquor is less than 3.3, sodium carbonate is slowly added at intervals until such a pH value is obtained. In either process, the leather sometimes receives a subsequent syntan treatment.

The one-bath system, however, has quite generally displaced the two-bath method. The liquor is made by reducing a mixture of $Na_2Cr_2O_7 \cdot 2H_2O$ and H_2SO_4 in equal proportions, with glucose. However, reduction by means of sulfur dioxide is a more recent method, and is more easily controlled.

The leather is dried, and may be split if necessary. Vegetable-tanned leather is also split for certain purposes. The splits are cuttings made by a knife resembling a band saw, kept sharp by constant contact with an emery wheel; the leather enters the machine at a constant rate, grain side up; when only one split is made, the upper piece travels on the table of the machine;[5] the lower one drops to the floor. With thick leathers a number of splits may be made. Each has the same lateral area as the original piece, but is thinner. An increase in the angle of weave of the bundles of leather fibers is associated with greater tensile strength and resistance to stretch; such a characteristic accounts for the increase of these properties from grain to flesh. Split leather is used for shoe uppers, insoles, bags, cases, straps, upholstery, gloves, etc. After splitting, the flesh side is shaved in a shaving machine. Light skins which have not been split may be evened in thickness by this process.

If the leather is to be dyed, the dye may be added to the fatliquor in some instances. The materials generally used for fatliquoring can be divided into three classes: soaps, raw oils and sulfated oils. The moist leather is tumbled in a drum with the fatliquor. It is important that the leather contain the proper amount of moisture; otherwise the oils may not distribute uniformly over the surfaces of all the fibers. Occasionally pigments are ground in the sulfated oils of the fatliquor.

Aniline dyes and dyewood extracts are generally used for dyeing leather. Dyewood extracts are: hematine, logwood, hypernic, fustic, etc. It is more difficult to reproduce shades on different types of leather with dyewoods than with aniline dyes. However, combinations of dyewoods and aniline dyes are very frequently used with satisfactory results.

A variety of materials are used in finishing leathers. Pigments and dyes are frequently incorporated in such products; they may comprise emulsions of waxes, shellac, casein, gums, nitrocellulose, resins, polyvinyl acetate, polyvinyl butyral, etc. The finish may be polished by friction in special machines and then placed between hot plates.

Sole leather is rarely made by the chrome process because it gives lower yields than vegetable tannage. Further, chrome sole leather loses its shape

[5] Invented in 1809 by Samuel Parker, of Newburyport, Mass.

and sometimes gets slippery. Vegetable tanning increases the weight of the leather; chrome tanning does also, but not to any great extent. Vegetable-tanned leather is sold by weight, chrome-tanned by area. An automatic machine measures the area in one passage of the skin; the total area is read off on a dial.

TABLE 137.—*Average annual production of hides and skins over the period 1942-1946.**

	Average production	Average imports	Percentage imports
Cattle hides	27,447,000	3,150,000	11.5%
Calf, sheep, goat skins	97,471,000	65,759,000	67.5%

* Tanner's Council of America.

Chamois skin is made from the inner split of a sheep skin, by the oxidation of fish oils in the presence of skins. The American Indians tanned buffalo skins by rubbing the brain into the dried skin. Velour leather is leather finished on the flesh side.

TABLE 138.—*Imports and exports of hides and skins, leather and leather manufactures (1946).**

	Lbs.	
Imports		
Hides and skins	224,721,348	$78,943,490
Leather		41,012,181
Leather manufactures, footwear and other		33,613,465
Exports		
Hides and skins	72,089,897	$11,826,620
Leather		24,227,667
Leather manufactures		60,194,581

* Tanner's Council of America.

In 1947, it was estimated that the shoe production in that year would total 470 million pairs. The average factory value of all shoes in the middle of the same year was placed at $3.84 a pair.

The by-products of the tanning industry are hair, which is used in plaster, for making hair felt for base rugs (an important use) and the small trimmings of the fresh hides, which are used for gelatin or glue.

GELATIN

The animal skin, connective tissue, tendons, and the bone contain collagen; as previously noted, the corium of the skin is 75 per cent collagen on a dry basis. Bones are one-third collagen by weight. Gelatin is valued for its power to hold many times its weight of water in the form of a semi-solid, called a gel, and for its power to retard or prevent the formation of crystals. A 3 per cent solution in water forms a jelly when cold.[6]

The skins used for making gelatin are rarely the perfect skins fit to make leather, but the trimmings in the hide house, and occasionally imperfect skins. The bones come mainly from near-by slaughterhouses and butcher shops, but also from long distances, such as heads from South American

[6] Gelatin with pH=4.6 acidity has maximum jellying power; above or below, it is less.

cattle; these often come with the horns attached. The horn pith gives gelatin, but not the horn proper. Hoofs yield no gelatin whatever. Sinews and tendons are suitable. Strict government regulations govern the selection of raw materials for the manufacture of edible gelatin, and require laboratory control of all the phases of manufacture. Glue is made from the same raw materials, but no government regulations apply.

The water employed in the preparation of gelatin must be as cool as possible in order to prevent excessive hydrolysis and the loss of jellying power which accompanies such hydrolysis. An advantage results from a pre-treatment of bones and skins with lime, for the preparation of the gelatin is easier, the temperature of 65° C. (149° F.) is warm enough, and the period required is shorter. Glue may be considered as gelatin which has been hydrolyzed further; its jellying power is low, also its water-absorbing power (imbibition), but its adhesive power is greater than that of gelatin.

Bones are first freed from grease by heating them with steam under pressure, releasing the pressure to a few pounds just before opening the kettle; the grease floats on the water and may be run off. It is utilized in soap-making. A better way is the extraction by means of a low-boiling petroleum naphtha, because there is no loss of gelatin-forming substance by this method. In many plants the bones are transferred over a belt conveyor which passes over a magnetic separator, placed at the turn of the belt. The bones drop off into a chute leading to squirrel-cage disintegrators where they are crushed, while any iron present is carried a short distance on the under side of the belt and then drops off into a receptacle. The crushed bones are hoisted to the top of a central tower by a bucket elevator and delivered through chutes to any one of a number of tanks. These tanks may be of various sizes; large ones are 20 feet in diameter and 5 feet deep; four tanks form a battery and are operated in series on the countercurrent principle. Cold dilute hydrochloric acid (5° Bé., 7.15 per cent HCl) meets the most nearly exhausted bones, while nearly spent acid overflows into the tank containing the fresh bones. The mineral matter of the bone, mainly calcium phosphate and carbonate, dissolves, leaving the organic matter, the collagen, with the original shape of the bone. Collagen so prepared from bones is called ossein. It may be treated further at once, or shipped to a factory. The latter procedure is sometimes economical if the ossein plant is located near a heavy chemical plant, so that the hydrochloric acid can be pumped through glass lines directly into the ossein plant, avoiding the rail transport of the acid. Skins do not need the preliminary acid treatment since their collagen is not masked by mineral salts.

The ossein is placed in 5-foot cubical concrete vats, of which there are several hundred, with slaked lime and water, and left there for a month or longer. The ossein swells and turns snow-white; the mucins and albumins are dissolved, and any remaining grease is saponified. At the proper time,[7] the ossein is removed to a rotary tank and washed with four changes; first with water, then with dilute hydrochloric acid, then twice with water; the cycle in the washer is one day. The ossein is then ready for extraction. Skins are treated in the same way; they become translucent.

[7] If the liming is continued too long, ammonia is evolved, and the material is spoiled.

The extraction of the limed ossein or skins is performed in tanks 4 feet broad and 4 feet deep, with a steam coil under a false bottom; the charge rests on the false bottom and thus does not come into direct contact with the coil. The water is maintained 60° C. (140° F.); in 8 hours a first extract containing 8 to 10 per cent gelatin is formed; it is filtered and cooled. A second extraction is made at 65° C. (149° F.); a good strength is obtained; the liquor is filtered and cooled. A third extract is made at about 75° C., (167° F.), but this will be too weak to jelly on cooling, so that it is concentrated in a vacuum to the jellying strength. The third run is darker and has a lower jellying strength; it is still edible, but is used for its water-retaining power chiefly, in marshmallow confectionery, for example.

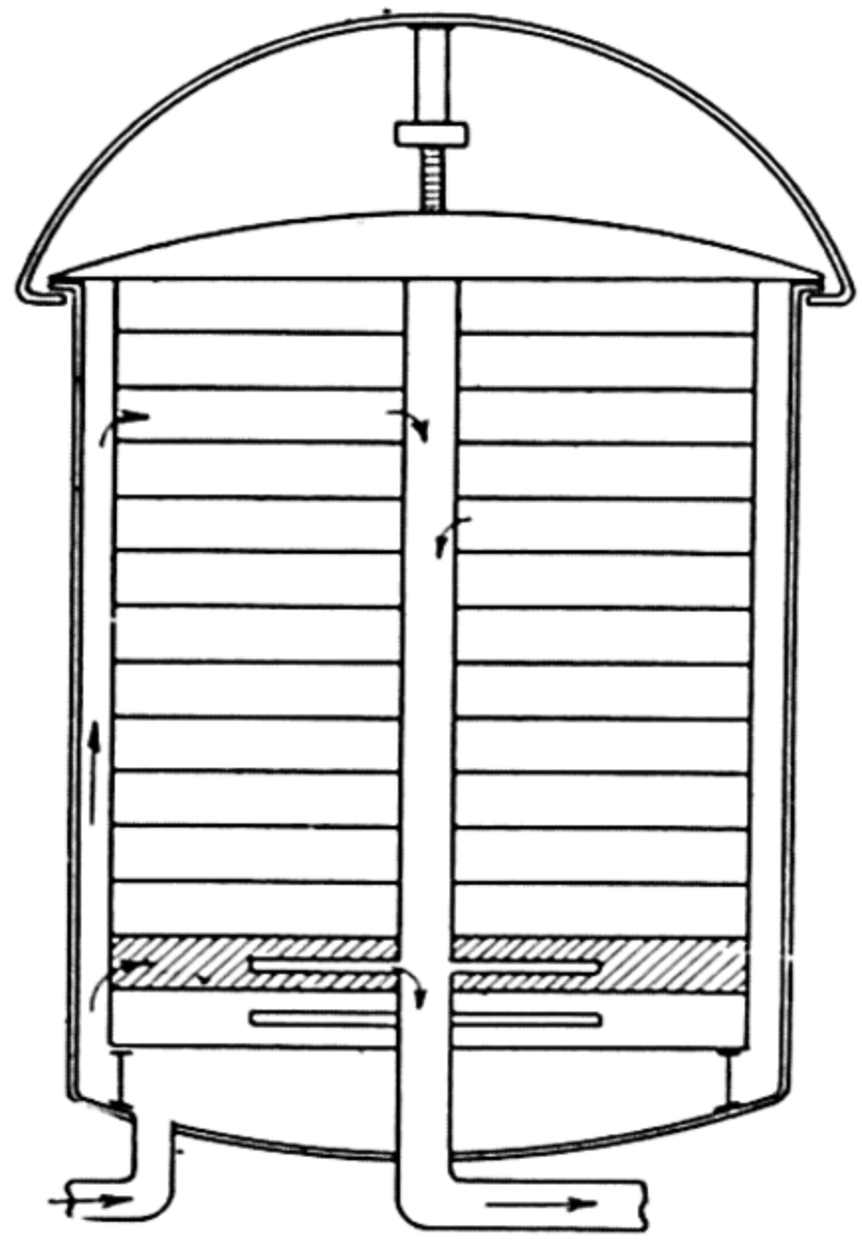


FIGURE 250.—Filter press for gelatin solution.

The reaction which takes place during extraction is probably as follows:

$$\underset{\textit{collagen}}{C_{102}H_{149}N_{31}O_{38}} + H_2O = \underset{\textit{gelatin}}{C_{102}H_{151}N_{31}O_{39}}$$

The filtration of the warm gelatin solution is done in a special circular filter, shown in Figure 250; the filtering medium is wood pulp; the solution passes from the entering space near the shell to the central channel. In order to reach the central channel a considerable layer of wood pulp must be passed; here the solution deposits the suspended particles, which cause cloudiness. The gelatin solution from the filter is placed in long steel troughs 6 inches deep and 6 inches wide, and cooled in refrigerated rooms. The resulting solid jelly is removed from the mold and cut by hand into strips one-half inch by 2 inches and 6 feet long. These are laid on "Monel" metal wire set in frames, stacked on small trucks and shoved into tunnels 70 feet long through which filtered air heated to 40° C. is pulled by an exhauster. The gelatin strip dries to a thin sheet which still contains about 10 per cent of moisture; this amount is not removed. The strips are usually ground to a coarse powder for greater ease in handling.

In some factories the filtered and partially cooled gelatin solution is congealed on the surface of chilled, revolving drums from which it is discharged in the form of a sheet onto a moving belt. The latter passes slowly through a drying tunnel from which dry, hard and transparent sheets emerge. The sheets are then ground to a powder.

In the Wheel Drying process,[8] the gelatin liquor is applied to the rotating drum by means of a V-shaped trough. One revolution of the wheel (or drum) requires approximately 45 seconds. After one turn, the dried gelatin is scraped from the wheel in the form of thin dry ribbons, which are reduced at once in an Abbé cutter into oatmeal flake form. The flakes are in the barrel ready for shipment within five minutes from the time the gelatin solution leaves the filters. The brief time practically prevents bacterial contamination.

Uses of Gelatin. Gelatin is a food accessory, easily converted into amino acids in the stomach; it is valuable also mixed with other foods because it disseminates the particles. With fats and oils it forms an emulsion which greatly facilitates the digestion; hence its use with meats and in desserts. Its use in ice cream is due mainly to its function as a protective colloid; it prevents the formation of crystals of lactose sugar and water during the storage period, at the temperature of $-10°$ F.; the proportion of gelatin sufficient for this result is 0.5 per cent. About 3000 tons of gelatin are used per year in the United States for this purpose. Its use in confectionary has been mentioned. All these uses together account for a yearly consumption of over 10,000 tons of edible gelatin in the United States.

Gelatin is used for capsules in the pharmaceutical houses; the hard two-piece telescopic capsules are gelatin alone; the flexible capsules contain glycerin also. In the manufacture of photographic plates, films, and moving-picture films, gelatin is used for the sensitized coating which holds the silver salts. It has many other minor uses.

When gelatin is made from bones, there may be obtained as a by-product dicalcium phosphate, or by using more lime, tricalcium phosphate; the former is used as a fertilizer, the latter in the potteries for "bone china." Calcium chloride is formed at the same time, and is usually wasted. Grease as a by-product has been mentioned.

Glue, and "Pellet Glue" Process

The manufacture of glue is identical with that of gelatin, except that the raw materials need not be selected with such care. The extraction of the glue stock (ossein, limed skins) may be performed in a single "boil," but four extractions of shorter duration are preferable; the liquor is concentrated to perhaps 15 per cent in vacuum condensers. This concentrated liquor is congealed in thin layers, and these are dried in a tunnel drier. A preservative is added to the concentrated solution (borax, formaldehyde); this cannot be done for edible gelatin.

Instead of drying the chilled strips of glue in tunnel driers, a method has been devised by Thomas K. Lowry, in which pellets of glue are formed

[8] U. S. Patent 1,318,464, Oct. 14, 1919, to Adolf Schweizer, now held by United Chemical and Organic Products, U-Cop-Co., Chicago 9, Ill.

and dried in a continuous process, eliminating the tunnel dryer and all the hand-labor it involves.[9] The 50 per cent glue solution is chilled, and forced through wire grills; a revolving knife cuts off (scrapes off) the protruding lengths into small pellets of equal size. The pellets pass through a three-stage system of drying. The first stage operates at 70° F. In this dryer stage, the pellets are kept in constant motion by automatic rakes. In the second stage the temperature is 100° F., and in the third, up to 130° F. Pellet sizes vary from $\frac{3}{16}$ to $\frac{3}{8}$ inch. The time in the first dryer is 3 hours,

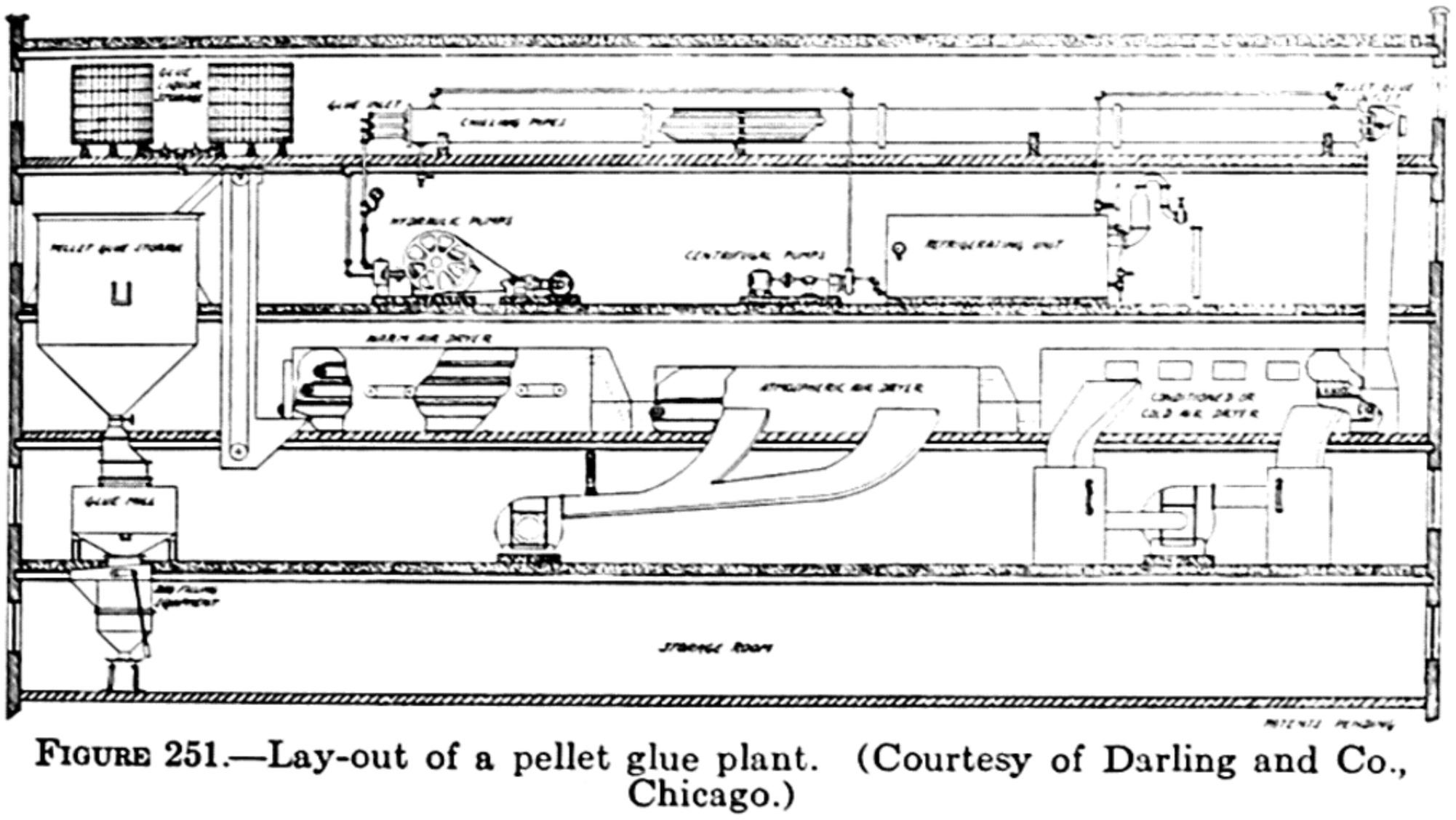


FIGURE 251.—Lay-out of a pellet glue plant. (Courtesy of Darling and Co., Chicago.)

in the second 6, and in the third 9. The total time is therefore 18 hours, instead of the 2 to 6 day period required by the older method. Figures 251 and 252 will help make the procedure clear.

Another method involves dropping the glue pellets into hot toluene.

The removal of grease from glue is essential, because it interferes with the adhesive power. A practical test is to make a 5 per cent solution, add a water-soluble dye, and paint this on a white board. Examination with a hand lens will reveal white spots if grease is present.

A strength test is made by gluing together two wooden blocks and after a definite time, placing them in a machine which measures the force required to pull them apart.[10]

Animal glue of the best quality is still unsurpassed for strength; it is used in furniture making, in veneering, book-binding, rug-sizing, in making the tips for matches, in sizing straw hats, for making sand paper, emery, Carborundum, and other abrasive papers. With waste leather, it makes imitation leather; ground cork is made into shapes with glue. A waterproof animal glue is made by adding tannins or formaldehyde.

Other Adhesives. Fish glue is made from the skins of the cod, cusk, and other fish; the washed material is heated with water and concentrated;

[9] *Factory and Ind. Management*, 82, July (1931), published by McGraw-Hill Book Co.

[10] Glue has maximum strength when its pH is 7.0; glue contains considerable calcium combined as calcium gelatinate.

phenol may be added and a little oil of wintergreen (synthetic) in order to mask the odor. Isinglass is the dry glue made by boiling the air-bladder of the sturgeon.

Fresh casein boiled with water has adhesive properties; once set, moisture does not weaken it. Starch paste or British gum is made by digesting starch with dilute acids. A solution of sodium silicate is an adhesive; it is not

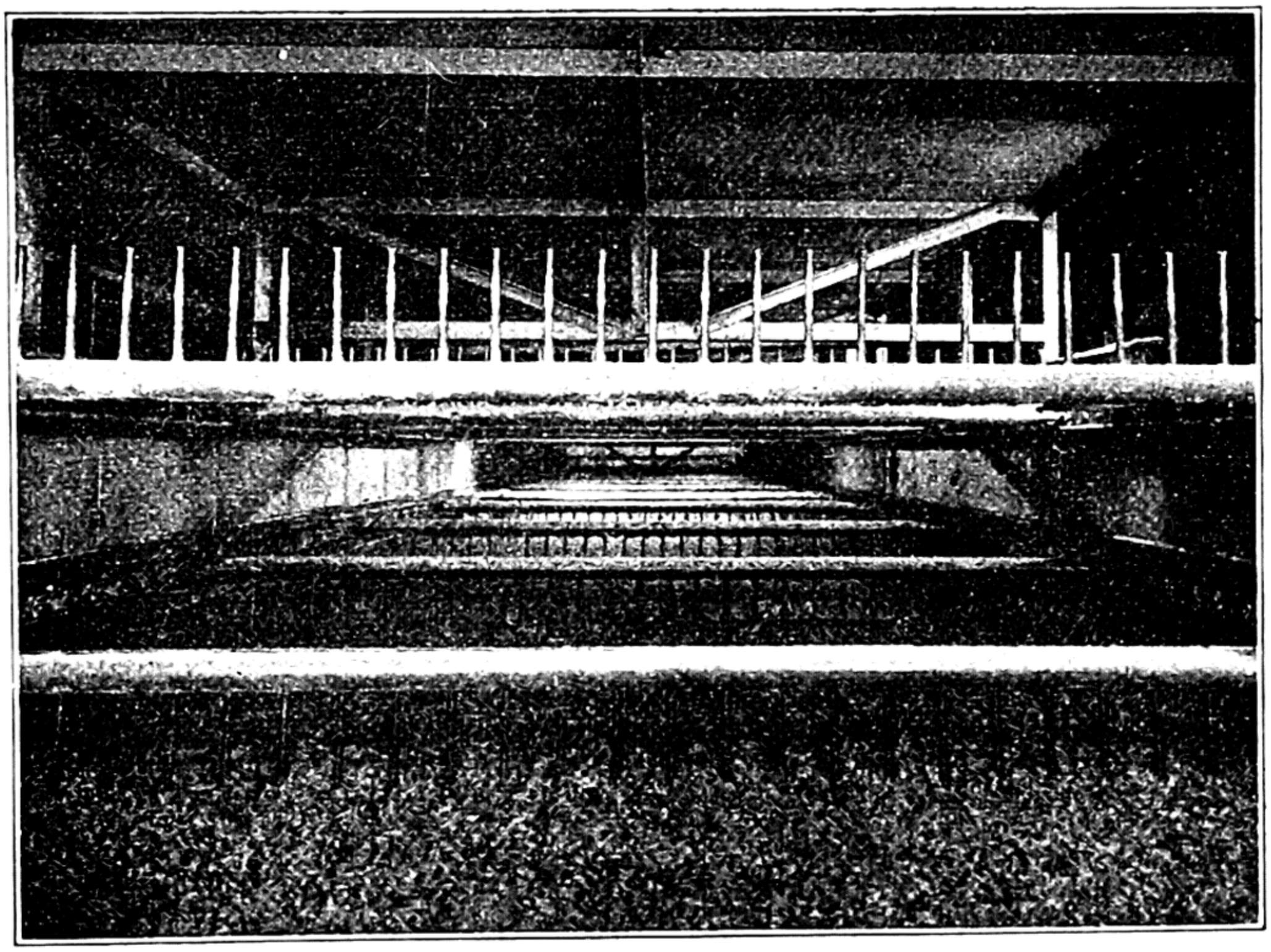


FIGURE 252.—The Thomas K. Lowry process for producing glue in the form of dry pellets. First stage dryer, operated at 70° F., with rakes on an endless chain. (Courtesy of Darling and Company, Chicago.)

strong, but sets quickly, and is valuable in the manufacture of cardboard boxes and corrugated paper. Mucilage is a solution of gum arabic or acacia in water. Marine glue is merely a name for a waterproof adhesive containing rubber, shellac, and naphtha.

TABLE 139.—*Production of gelatin and glue in the United States (1946).**

	Pounds
Gelatin	
edible	22,872,796
technical, pharmaceutical, photographic	4,736,804
Glue	
Bone glue	61,275,928
Hide glue	60,863,528

* "Facts for Industry"; three months' total extended to twelve.

The production of animal glue from July 1944 to June 1945 was 152,953,000 pounds.[11]

[11] Facts for Industry.

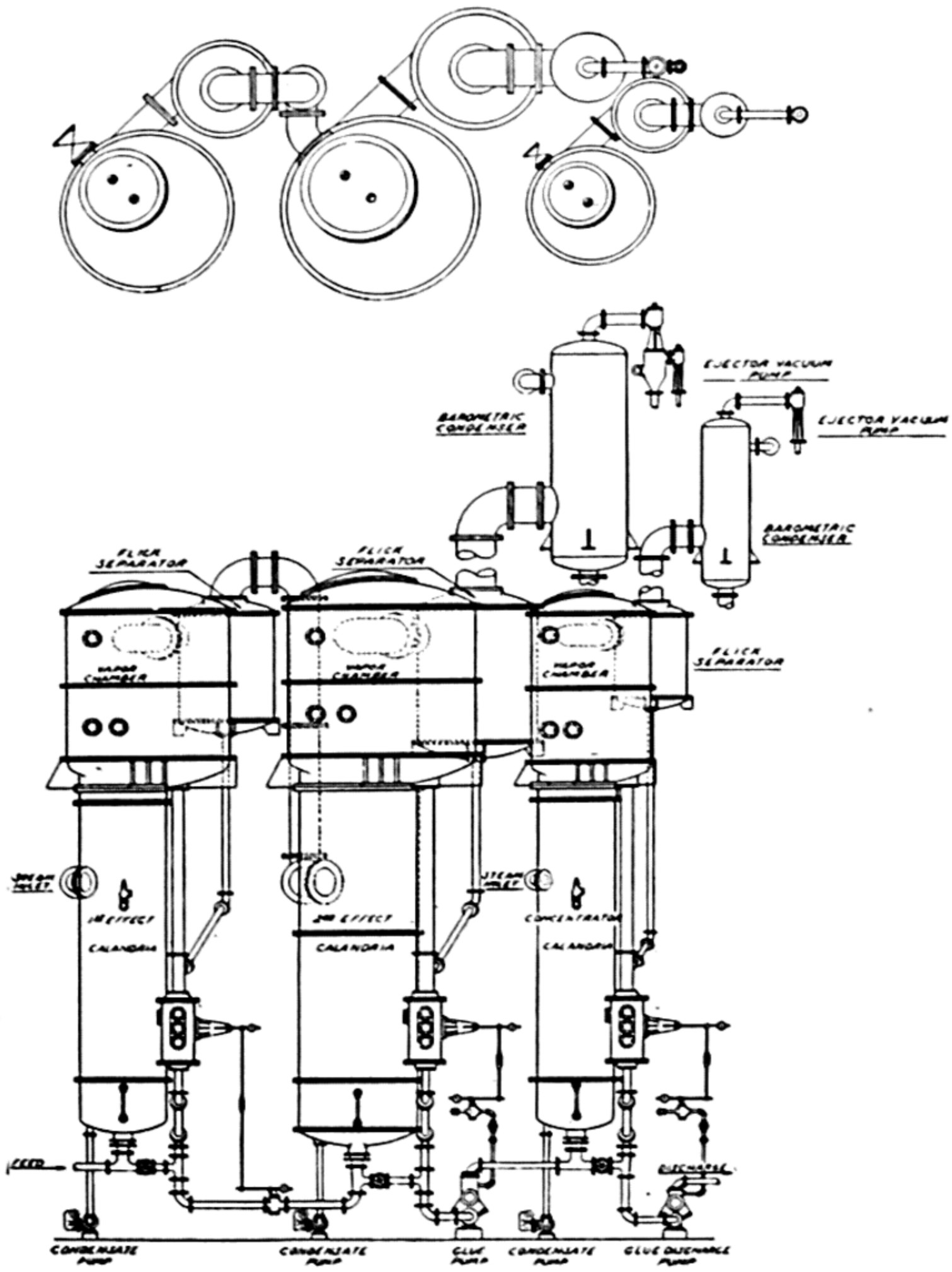


FIGURE 253.—A W&S continuous glue evaporator with a double effect evaporator followed by a concentrator, High Velocity, Long Tube, One Pass, Climbing Film Type. Note from the plan the tangential connection from vapor chamber to Flick Separator. The three vessels differ in size to meet the changing conditions of gravity and viscosity of the liquor. The high vacuum provided permits the use of comparatively low temperatures; the period of heating is short, the liquor passing through the unit (all vessels) in 10 minutes. (Courtesy of Wurster and Sanger, Inc., Chemical Engineers, Chicago, Illinois.)

The quotation for gelatin, silver label, is $1.25 a pound, in containers; bone glue is $0.22 a pound; hide glue is $0.25 to $0.28 a pound, depending upon jellygrams rating (Dec., 1948).

Colloid Chemistry. The study of tanning, and of the nature of glue is an important part of the branch of chemistry called *colloid chemistry* which includes in its considerations the combinations due to forces between surfaces, and at those surfaces, such as droplets, grainlets, or bubbles of submicroscopic dimensions, in a gas, liquid or solid; pure chemistry concerns itself primarily with forces and events within atoms and molecules, and between them. For the combination of tanning agents with the collagen of

corium a simple reaction cannot be written. In the tanning process, the tanning agent is more or less irreversibly fixed by the hide protein whereby its hydrophilic centers are changed into hydrophobic (dehydrating, water-repelling) groups. Resistance of the product toward the action of proteolytic agents is thus acquired.

It was the substance glue, the first one studied with respect to surface forces, which gave its name to colloid chemistry.[12]

Other Patents

1,848,506, thiophenol tanning and mordanting agents; 1,851,021, producing water-soluble tanning agents which comprises condensing a methylol compound of a monohydric phenol with resorcinol at a temperature below 50° C., in the presence of water and a condensing agent; 1,844,018, a new tanning composition comprising the halogenated reaction product of sulfite cellulose and hydrogen peroxide; 1,895,446, process for producing a transparent clear bone glue or bone gelatin solution; 1,895,433, on improving water-resistance of casein glues, by treating with a polymerized acetaldehyde; 1,858,193, manufacture of vegetable-tanned sole leather; 1,881,763, process for cold dressing and drying leather; 1,753,694, leather finishing compound consisting of crude oil, sweet oil, cod liver oil and glycerin; 1,744,756, a leather-stretching and tacking machine; 1,892,599, a process for the manufacture, sterilization and puffing of gelatin; 1,310,148, apparatus for stretching and drying leather. On pre-tanning and tanning of leather, U. S. Pat. 2,316,741 and -0; 2,205,883; 2,309,187 and -8; Brit. Pat. 569,396 and -5.

Reading References

"A brief history of leather and a description of tanning," distributed by the American Leather Producers, Inc., 41 Park Row, New York.

"Glue and gelatin," Jerome Alexander, New York, Chemical Catalog Co., Inc., Reinhold Publishing Corp., 1923.

"The chemistry and technology of gelatin and glue," R. H. Bogue, New York, McGraw-Hill Book Co., 1922.

"The manufacture of leather," W. K. Lewis and R. H. W. Lord, *Trans. Am. Inst. Chem. Eng.*, 26, 208 (1931).

"Synthetic tannins, their synthesis, industrial production and application," Georg Grasser, translated by F. G. A. Enna, London, Crosby Lockwood and Son, 1922.

"Modern practice in leather manufacture," J. A. Wilson, New York, Reinhold Publishing Corp., 1941.

"Casein and its industrial applications," 2nd ed., Chapter 8, "Casein glues," New York, Reinhold Publishing Corp., 1939.

"The chemistry of leather manufacture," Drs. George D. McLaughlin and Edwin R. Theis, Reinhold Publishing Corp., 1945.

"Tanning processes," August C. Orthman, Chicago, Hide and Leather Publishing Co., 1945.

"Fundamentals of leather science," D. Woodroffe, A. Harvey, publisher, Croydon, England, 1941.

"The chrome tanning process," Dr. E. N. Merry, A. Harvey, publisher, London, England, 1936.

Journals of the American Leather Chemists Association, published at Easton, Pa.

Journals of the International Society of Leather Trades' Chemists, published at Croydon, England.

"Stiasny Festschrift," Darmstadt, Germany, 1937.

"Gerbereichemie," E. Stiasny, Theodor Steinkopff, Dresden, Germany, 1931.

[12] The Greek word for glue is "kolla."

Photography serves us in countless ways. Besides being a medium for the fine arts, for individual portraiture, for visual education and entertainment, and for the reproduction of books and magazines, it is an indispensable aid to science. Astronomers rely on it for their studies of the heavens; chemists for analysis of molecular complexes; physicians for diagnoses. It also aids the physicist in determining microstructures and the metallurgist in examining defects in metal objects. The development of aerial photography during the war was noteworthy. Altogether, photography has added immeasurably to human knowledge and pleasure during the last 150 years.

Chapter 37*

Photographic Films, Plates, and Papers; Color Photography; Lithography

Photographic Films

Photography has passed through several stages on the way to its present position of almost universal service. Originally developed as a means of quickly recording stage settings (Daguerre), it became a replacement for painting, a hobby. With the introduction of gelatin and later of the flexible celluloid film, the present dry plate and roll film became possible. Constant study led to improvements which allowed exposures of very short duration. Pictures of landscapes, perfect and sharp, are taken as a matter of routine from airplanes traveling 100 miles per hour, with exposures of one three-hundredth second.[1] Astronomy relies on photographic records for most of its evidence for the location of stars, and for the determination of their movement toward or away from the earth (Doppler effect). Rapid chemical analysis by the photographic record of emission spectra of alloys and compounds, in the ultraviolet as well as in the visible region of the spectrum, is routine. The selective absorption of x-rays by teeth, bones, foreign metal pieces, and coated animal organs, gives opportunity for photographic records which are the basis of modern diagnosis and surgery. Portraiture has become a fine art. Engineers' drawings and bulky documents are recorded on microfilm, and may be stored in a small space, which at the same time is safe from fire and theft.

In a war emergency, a camera with a telephoto attachment, carried aloft by a reconnaissance plane, observes in an instant more than the human eye could in an hour, and yields its information, independently of memory, in a way which allows leisurely and repeated study. It was such a study which convinced a woman operator in the Royal Air Force that a V-2 rocket-launching site was located in a certain spot on the European continent. A

* Based largely on consultations with Mr. Raife G. Tarkington, Research Laboratory, Eastman Kodak Company, Rochester, N. Y.

[1] Erie County, N. Y., has been photographed from the air, so that a complete map showing roads, rivers, bridges and buildings is available; the elevation of the airplane was 9500 feet. In Connecticut, the towns of Westbrook and of Deep River have enlarged airplane views of their whole townships; the taxing unit uses the pictures to reveal unreported structures. Aerial photographs at speeds of 1000 miles per hour have been obtained (two planes flying in opposite directions at 500 miles per hour).

bombing expedition by the Royal Airforce followed, and the launching site was indeed destroyed. The atomic bomb explosion at Bikini (test Able) is recorded photographically for all time (pictures in Chapter 50).

Returning to civilian life and the applied sciences, metallography, the study of the fine structure of metals and alloys, is 99 per cent photographic. The film roll, the film pack, the color film for color photography by the amateur, have greatly stimulated photography as a hobby. The talking moving picture in "Technicolor" is for the moment, the latest word in the development of photography.

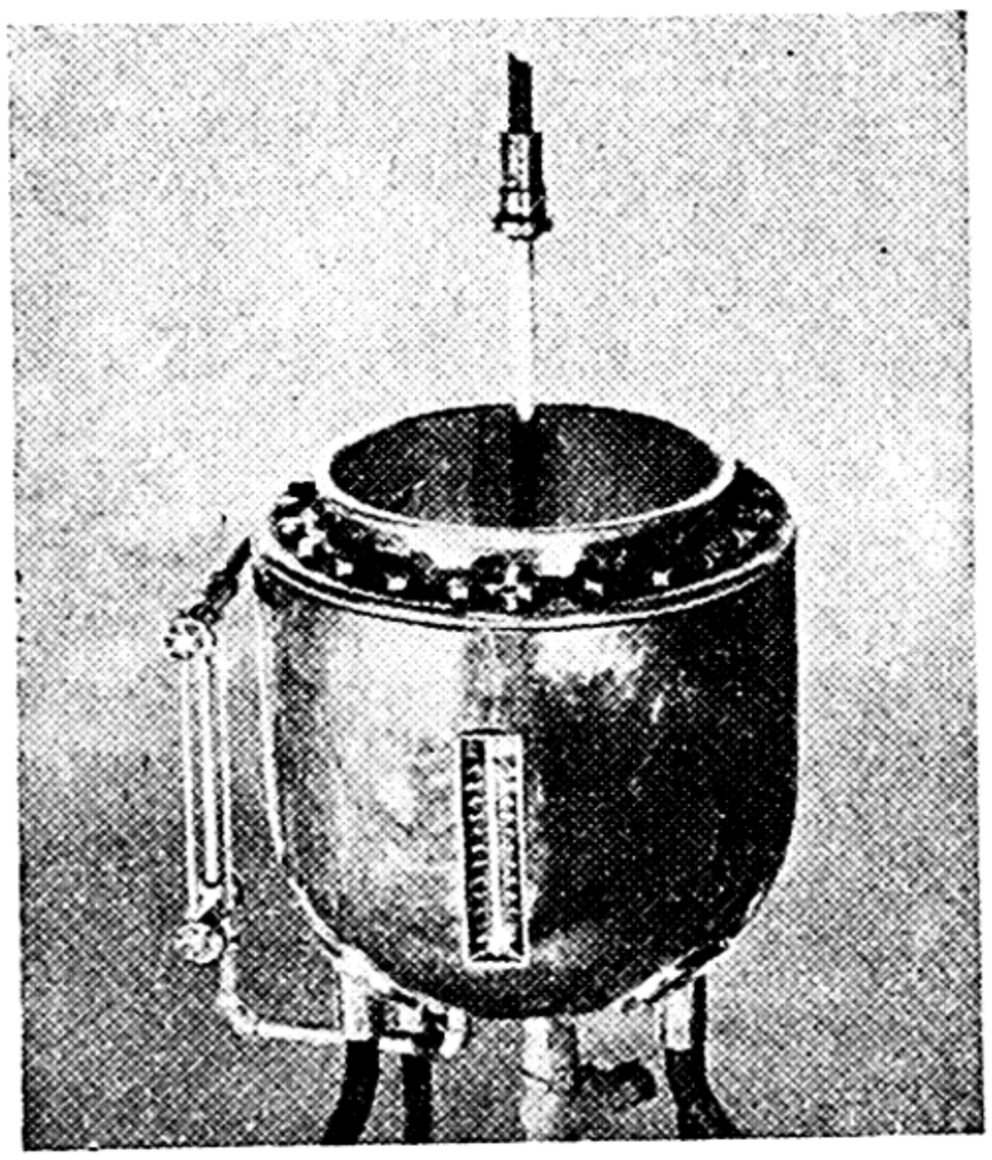


FIGURE 254.—An emulsion kettle made of silver, with a copper jacket. (From "Photography," by C. E. K. Mees, p. 40, The Macmillan Co., N. Y., 1945.)

All the applications of photography listed above depend upon the action of light on silver bromide. In blueprints, much less expensive iron salts are used, and the development is simple and cheap, so that blueprints are commonly chosen for the recording of drawings and tabulations of all kinds.

The present dry plate and dry film were preceded by a plate which was sensitized just before exposure, and without drying (wet plate); this method is still practiced in certain branches of commercial work. Still another method of photographing depends upon the hardening action of light on albumen containing sodium dichromate; this principle is applied on a large scale in lithography by the zinc plate method. Photosensitive glass is described in Chapter 11.

The Light-sensitive Emulsion. The light-sensitive portion of dry plates and films is the coating of gelatin in which mixed crystals of silver bromide and iodide are dispersed. The gelatin coating is the essential part, the glass plate or the flexible film merely furnishing a suitable support.

The gelatin used is made from calf skins.[2] In an emulsion kettle made of silver, and copper-jacketed, a solution of potassium bromide with some potassium iodide is placed; between 1 and 5 per cent of gelatin is added, and into this new solution, a lukewarm water solution of silver nitrate is run.

[2] Chapter 36.

The silver bromide which forms remains in suspension by virtue of the protecting action of the gelatin. The resulting "emulsion" undergoes a "first ripening," then a washing, followed by addition of enough gelatin to raise the concentration to 10 per cent; after this a second ripening (the "after ripening") is performed. "Ripening" takes place as the emulsion is held in its kettle for a period of time at a selected temperature.

The first ripening of a photographic emulsion establishes the grain distribution of the silver halide. There are two methods of ripening: the neutral method and the method using ammonia. With the latter, ripening occurs more quickly and at a lower temperature than with the neutral method. Emulsions in which ammonia is employed, are ripened at a temperature not exceeding 50° C. (122° F.), while neutral emulsions can be ripened at a temperature between 70 and 90° C. (158 and 194° F.). The time of ripening is usually less than one hour. The higher the temperature and the longer the time of ripening, the greater the range of grain size produced and the larger the maximum size of the grains. At this stage a photographic test of the emulsion would show that it has very little sensitivity and gives very poor contrast.

The emulsion is now washed while in the form of "noodles," in a solution of a polyvalent salt, to remove the potassium nitrate formed as the second product of the reaction

$$AgNO_3 + KBr \rightarrow AgBr + KNO_3.$$

In order to form the noodles, the soft jelly is placed in cheesecloth bags and pressed under water; the stringlets of emulsion formed in the cold salt solution are the "noodles." Another way to shred the emulsion jelly is to force it through the holes in a metal plate at the bottom of a hydraulic press. A solution of a polyvalent salt is used for washing, because it does not swell the gelatin as pure water would.

For the "after-ripening," the washed jelly is melted and the last of the gelatin is added. The remelted emulsion is held in its kettle at a temperature of 50° C. (122° F.) or higher, when contrast and sensitivity increase very rapidly. The heating is continued until the emulsion attains contrast and speed normal for the type of emulsion being prepared. The time of after-ripening is usually less than an hour. At the time of remelting, there are added to the emulsion some alcohol, a little thymol as a preservative, some chrome alum and some potassium bromide as a retarder; all these substances are in solution. The alcohol helps the flow of the emulsion, and the chrome alum hardens it.

There are other factors which affect the speed of the plate. For example, the greater the proportion of silver salts to gelatin, the faster the plate; furthermore, silver bromide with iodide addition is more sensitive than bromide alone. A "fast plate" or film requires a short exposure, a "slow plate" a long one. In the usual emulsion, the silver salts are 30 per cent of the total.

The film base may be cellulose nitrate suitably plasticized to form a flexible film, or cellulose acetate made plastic enough to form a sheet. Cellulose nitrate film base is excellent in all ways except one—it is inflam-

mable. Cellulose acetate film base is not inflammable; it will burn, but not readily, and it has become a safety film. Moving picture film, especially when intended for amateur home movies, uses the cellulose acetate base. One type of film base-forming machine has a large cylindrical wheel which turns slowly; its surface is plated to make it perfectly smooth. The solution of cellulose nitrate in solvents, with plasticizer, is fed to the wheel through a wide slot; by the time the wheel has made a little less than one turn, enough

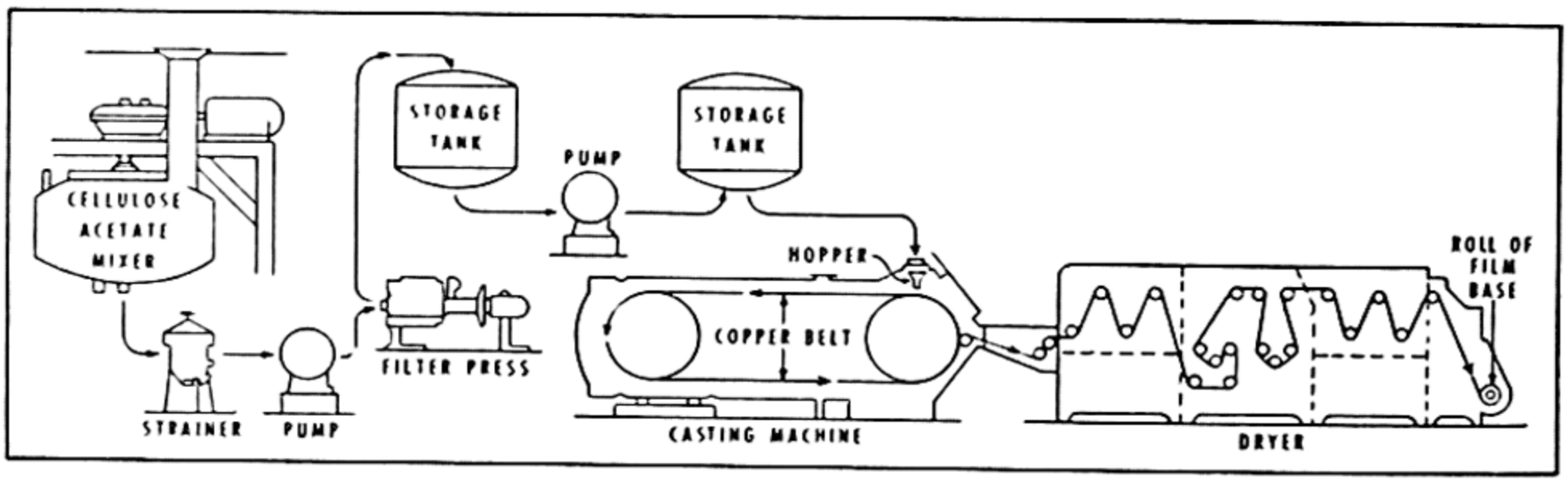


FIGURE 255.—Sketch for the manufacture of the Ansco film base. The casting machine has a copper belt 48 inches wide and 50 feet long. The cellulose acetate (or nitrate) dope with plasticizers is fed to the belt from a long narrow slit in the hopper. (Courtesy of Esso Oilways, 15 W. 51 St., New York, N. Y.)

solvent has evaporated to allow the film to set, so that it can be transferred on other rollers to a dryer. The dry film base is wound in rolls containing 1500 feet or more.

The film base is coated with emulsion by passing it under a roller which dips in a trough containing the warm emulsion. The coated film travels into a cold-air chamber, where the emulsion sets, and then to a dryer. The dry, coated film may then be wound in rolls from which the various forms of finished film are prepared.

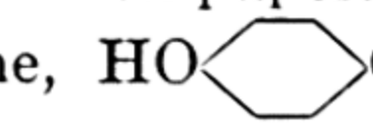
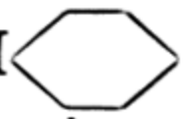
Photographic plates are made by coating glass with the same type of emulsions as those used for films. The glass is cleaned, washed, coated with a very thin layer of gelatin, dried, then placed on a belt which carries it under an emulsion spreader; the belt travels on rolls kept warm with hot water. The coated glass passes to a belt travelling on cooled rollers, and there is chilled so that the emulsion sets. The plates are then placed on racks in a dryer. Drying for plates and films must be uniform, and uninterrupted.

Photographic paper is coated in much the same way as plates and films, but as a rule the emulsion used is much less sensitive. A specially made paper is coated with a white pigment, usually blanc fixe, then examined for defects, and finally coated with the light-sensitive silver salt emulsion in gelatin. Most paper emulsions are made with silver chloride and their processing is simpler than that of the negative emulsions; the exception is the relatively rapid bromide paper for enlarging. Making the emulsion, ripening it, coating plates and films as well as paper, and drying, is performed in filtered light, which may be orange, deep red, green or entirely absent.

Camera. The plate or film is exposed in the camera which for short exposures must have a lens allowing maximum light to enter, and a good

shutter. The larger the lens diameter, the more light it will admit. Improvements in lenses and shutters have kept pace with the advances in plate and film manufacture. For moving pictures a special camera is obtainable for amateur use (with 8- or 16-mm. film, instead of the standard 35-mm. width).

Developing and Fixing. The exposed plate (or film) is placed in an alkaline developer in a darkroom; the developer causes metallic silver to form at the spots affected by the light, the amount of the silver developed being a function of the intensity of the light and its duration. After the picture has appeared and begins to disappear, the plate is removed from the developer, washed in water, and placed in a solution of sodium thiosulfate, commonly called "hypo" (Chapter 4), which removes the unchanged silver salt, thus fixing the image. After washing, the plate is dried, and is now the negative. From the negative, a positive is printed on paper.

The alkaline developers are hydroquinone, HO  OH; pyrogallol, 1,2,3-trihydroxybenzene; metol, or methyl-para-aminophenol, OH  $NH \cdot CH_3$, in the form of sulfate; and eikonogen, the sodium salt of α-amino-β-naphthosulfonic acid. These are called alkaline developers because they are used in a solution of sodium carbonate. Sodium sulfite is also added to prevent oxidation by the air, and a little potassium bromide to retard the development of any unaffected silver bromide. Amidol is used without alkali; it is diaminophenol hydrochloride [$1,3,4\text{-}C_6H_3 \cdot (OH)(NH_2)(NH_2HCl)$]. One developer may give a green shade, another a brown shade of black; as a rule, a mixture of two developers is used to give deep blacks.

For moving pictures, it is convenient to make a negative, from which any number of positive films may be produced.

The explanation of the action of light on the rapid photographic plate or film is as follows: In the silver bromide lattice (which makes up the grain or crystal imbedded in the gelatin) there are sensitive centers due to the presence of molecules of silver sulfide. Wherever there is a silver sulfide molecule, the normal lattice is distorted, for silver sulfide does not fit into the Ag^+ and Br^- system. Each point of distortion acts as a trap for electrons liberated anywhere in the silver bromide crystal by the photoconductance effect. The trapped electrons concentrate free silver ions on the speck and thus form silver atoms. The silver sulfide specks act merely as nucleating points for the silver atoms produced by light striking the crystal anywhere on its surface.

The silver sulfide has its origin in an impurity of the gelatin, present in exceedingly minute amounts, called allyl mustard oil; this substance reacts with silver bromide to form, after several intermediate compounds, silver sulfide.

The invisible latent image consists of a minute amount of metallic silver, and this slight amount becomes the nucleus for further deposition of such silver as the developer produces from the silver bromide.

The photographic dry plate prepared from the gelatin emulsion of silver bromide is sensitive to wave-lengths in the green, blue and violet, the region of 500 mμ to 400 mμ. By adding a dye such as erythrosine, ethyl red, pina-

cyanol, orthochrom, to the emulsion, the resulting plate or film becomes sensitive to yellow, as well as to green, blue and violet; such plates are called *orthochromatic.* By the use of polymethine dyes, plates sensitive to the entire visible spectrum are produced, and are known as *panchromatic* plates.

To photograph in the infrared, in the region between 700 and 800 mμ, kryptocyanine is the dye added to the emulsion; for the region beyond 800 mμ, as far as 1014 mμ, a plate sensitized with neocyanine will record the light. In this fashion, the photographic plate can reveal light waves invisible to the eye, and longer in wave-length than red light.

In the ultraviolet, good records are obtained with panchromatic, or ordinary plates in the region between the violet and 320 mμ. Below 320 mμ, to about 200 mμ, the plate may be made sensitive by covering it with a thin layer of petrolatum, so that the invisible light of wavelengths shorter than violet may also be caught by the photographic plate.

An additional striking advance has been made. After a highly sensitive plate has been exposed, it may be bathed in a solution of phenosafranin, with the result that its sensitivity to light is reduced so considerably that it may be developed by dim light with practically normal results. This is called desensitizing.

Wet Plate Process. The wet plate process is older than the dry plate, but is still used for commercial work, such as in lithographic plants. The same glass can be used over and over, after the negative is no longer needed. It is coated with collodion (pyroxylin dissolved in ether-alcohol) containing potassium bromide and some iodide, dried for a few moments, and bathed in a solution of silver nitrate; the excess solution is allowed to drain off, and the plate is ready for exposure. It is developed by means of a solution of ferrous sulfate in dilute sulfuric acid; the negative image appears in metallic silver, as with the dry plate. The unchanged silver bromide is removed by a dilute sodium cyanide solution. The negative may be intensified by means of copper sulfate and potassium iodide solution, followed by silver nitrate; or it may be reduced by bleaching in potassium iodide-iodine solution and reacting with very dilute sodium cyanide. Finally a solution of sodium sulfide converts the image to a jet black.

In dry-plate photography, a faint negative may be intensified by a solution of mercury bichloride, followed by ammonia. A picture which is too dense, on the other hand, may be reduced with Farmer's solution, which contains "hypo" (sodium thiosulfate) and potassium ferrocyanide. There are several other formulas. A solution of ammonium persulfate is a reducer. For the complete removal of the developed silver, as in a reversal, a solution of potassium permanganate and sulfuric acid is used.

Color Photography

The earlier color photography employed among others the "additive" principle. An example is the Lumière plate, whose microscopic dots of red, blue and green were "added up" by the eye to produce the colors in the original. Recent developments are based on the "subtractive" principle, of superior value: layers of blue (cyan), magenta and yellow dyes subtract

certain wave lengths of light from white light, permitting the right amount of red, green and blue, respectively, to pass and reach the eye. "Kodachrome," "Kodacolor," "Ektacolor," and "Ansco" Color Film, are examples of the application of the subtractive principle.

"Kodachrome" film is made directly into the final transparency in color (a positive). The film is available in sizes for miniature cameras, for motion-picture cameras (16 mm.), and in sheet form, as for example "Kodachrome" Professional Film. There are modifications to fit the kind of light used, such as Daylight Type; Type A for use with Photoflood lamps, with approximate color temperature of 3400° K; Type B, "Kodachrome" Professional Film, employed with tungsten lamps, 3200° K. In general, "Kodachrome" does not require a light filter of colored glass in front of the lens.

The "Kodachrome" is composite; it is made up of three layers of silver salt emulsions (separated by gelatin) which have been treated to make them sensitive to light of different colors, that is, different wave lengths. The first and topmost layer is sensitive to blue light only, which it records. A yellow filter layer, a special layer not mentioned before, stops every trace of blue light at this depth. This is necessary because the two emulsions below, which are sensitive to green and red, respectively, are also sensitive to blue, as all photographic emulsions are. The second layer is sensitive to green light, and records it. The third and bottom layer is sensitive to red.

The exposed film is placed in a regular solution which develops the silver image throughout. It is a negative image. The film is then exposed through the base to red light, thus affecting the remaining silver halide in the bottom layer, after which it is developed in a bath containing both the developer and a cyan coupler. A positive picture in cyan dye is produced by the action of the oxidized developer molecule on the coupler. The top layer is now exposed to blue light, and is developed in the presence of a coupler which produces yellow, so that there results a positive image in this dye. The middle layer is developed in the presence of a coupler so selected that a magenta dye is produced. It should be noted that the secondary exposures to special lights and subsequent steps constitute a reversal of the picture. The negative silver image is still present at this stage. It is now removed along with metallic silver produced by the second exposure, as well as any undeveloped silver halide. The final image, therefore, consists of dyes only. The special yellow filter layer has also been removed in the processing. In spite of its complexity, "Kodachrome" film is almost as thin as the regular silver salt emulsion for black-and-white photography.

"Kodacolor" film is very different in details from "Kodachrome," although based on the same general principles; it is available as roll film for amateur cameras, and no filter is used in front of the lens. "Kodacolor" is made into a negative in colors which do not resemble those in the original, but are complementary; from this negative, positive color images on paper are produced in a supplementary operation.

"Kodacolor" film has a light-sensitive pellicule which again is composite; it has a top layer sensitive to blue, a second layer sensitive to green, and a

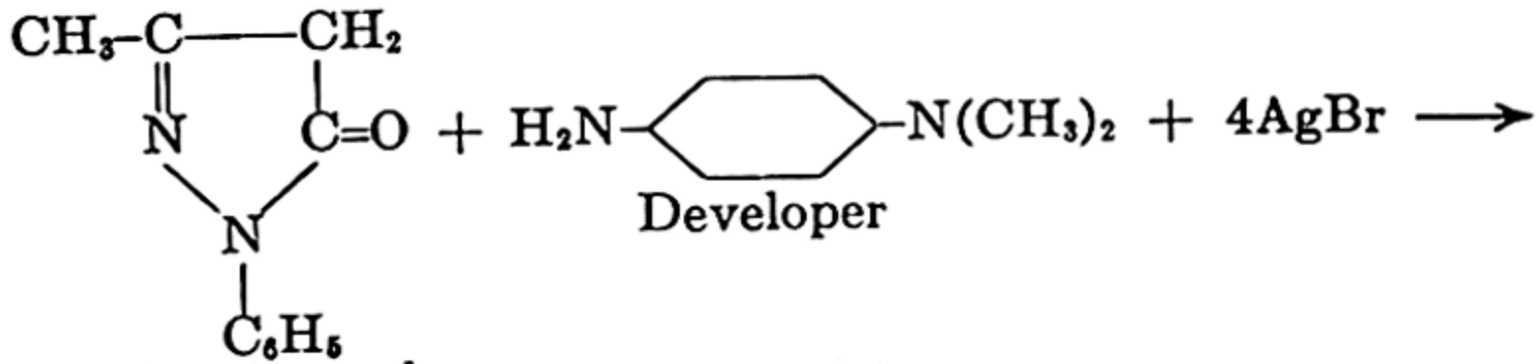
bottom layer sensitive to red. Under the top layer, there is the stop-all-blue layer, already mentioned; underneath this is another special "mask" layer. Each of the three color-recording layers contains a proper, specific coupler, which after reaction produces the dye of the desired color. The coupler is present in the microscopic globules of an organic carrier, in which it is dissolved. The globules are fixed in their location and cannot wander.

As the silver salt reacts with the developer (paraphenylene diamine or one of its derivatives) there are formed metallic silver and a second product, the oxidized diamine. The latter dissolves in the organic carrier and couples with the selected body therein, forming the dye. A coupling reaction takes place in each layer, with production of the different dyes. In the next step, the silver image in the color layers is removed, but not the unaffected silver bromide. In another processing step, a negative image of the dyes in the two lower layers is formed in the mask layer by exposure to light through the film base. The unchanged silver halide is now removed, and the film washed and dried. This is the final negative, with complementary colors in the three sensitive layers, plus the silver image in the mask layer.

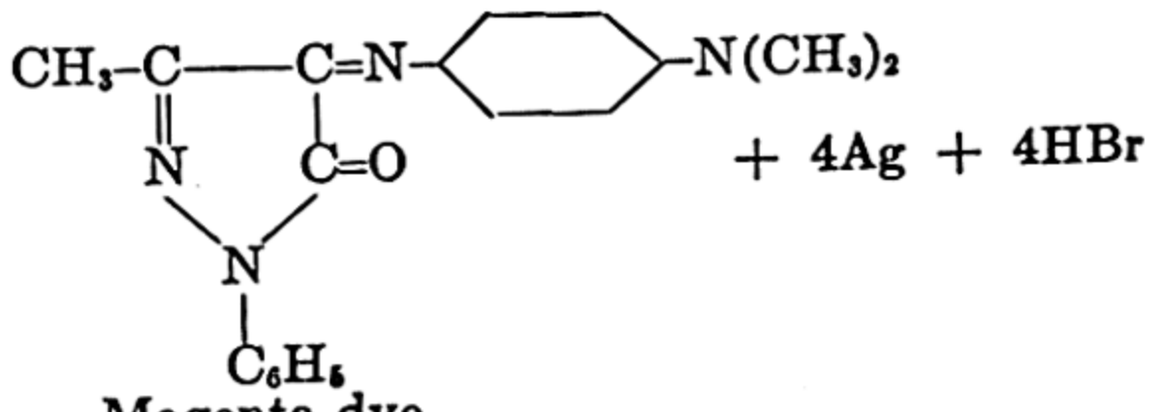
The effect of the mask, in brief, is to improve the quality of the print. In general, the combination of a positive of one color separation with a negative of another is termed "masking."

"Kodacolor" film negative is printed on paper having emulsion layers similar to those in "Kodacolor" roll film, but without the mask. The exposed paper is processed in a similar way, and there results the final print in the form of a positive in color.

Recent development work [3] has led to the introduction of colored couplers instead of uncolored ones in the original film, as a means of correcting defects resulting from certain overlapping in the absorption of the dyes in the "Kodacolor" negative.[4] The colored couplers are so chosen that they bring about this correction; moreover, their coloring group (the chromophore) is ejected and replaced by the developer group when the coupling reaction takes place. Two reactions illustrating this development are given below; they will serve at the same time to clarify the coupler reactions previously mentioned.



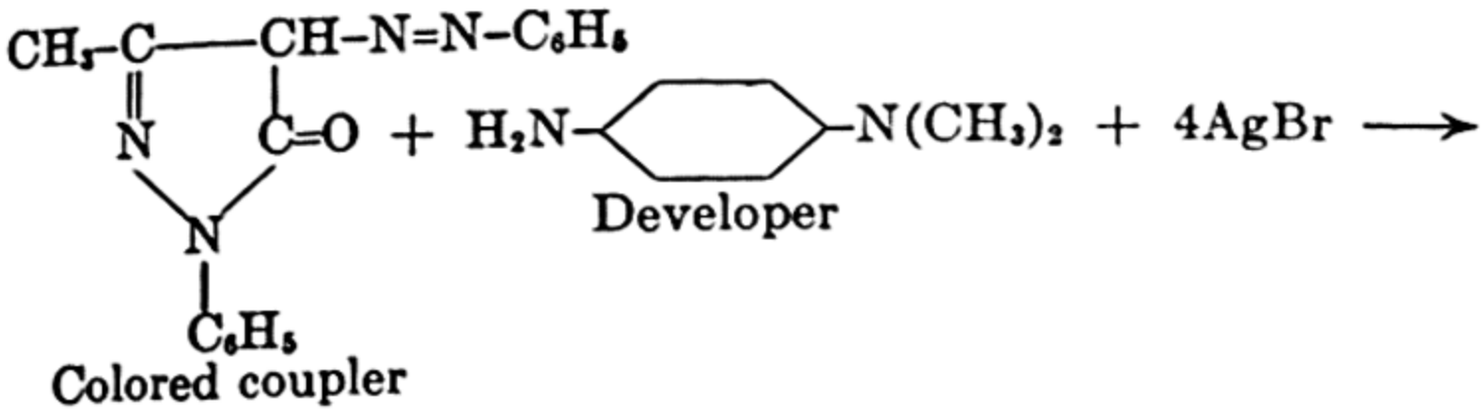
Uncolored coupler

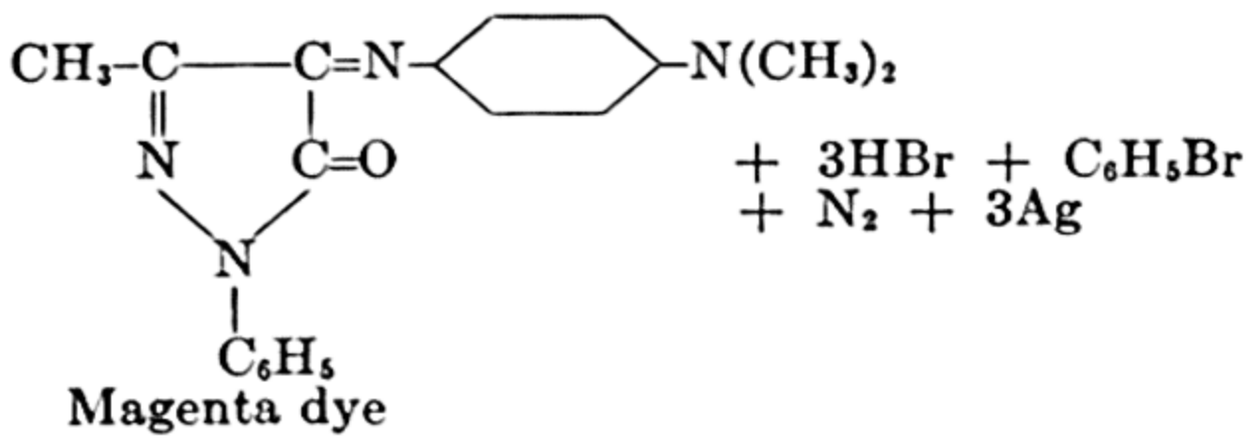


Magenta dye

[3] "Colored dye-forming couplers in subtractive color photography," W. T. Hanson, Jr., and P. W. Vittum, *J. Photographic Soc. of Am.*, 13, 94 (1947).

[4] All dyes used in subtractive color film exhibit overlapping absorption.





Any unreacted colored coupler molecule persists throughout the processing, and is present unchanged in the final image.

Since August 15, 1949, under the name of "Ektacolor" film, these improvements have become available to the public. "Ektacolor" is a color film which has automatic masking. It produces a negative, from which prints on white paper are made.

Perhaps a few more words will be welcomed by the reader interested in this fascinating topic. The dyes are imperfect, hence the need of masking. Consider the cyan dye image; it should absorb red only, but it absorbs some blue and green, which it would not, were it a perfect dye. To correct, there is introduced an equivalent blue and green absorption all over the film, by means of the colored couplers. In printing, a source of light is used which is corrected to meet this absorption; the effect of the unchanged couplers is thus nullified, as well as the unwanted absorption in the same region by the cyan dye. Similarly, the unwanted absorption of the magenta dye is also nullified. The imperfect dyes have been to function as if they were perfect. The colored couplers are actually a colored mask *in situ*. "Ektacolor" film in its unexposed portions (and state) is orange.

Dye Transfer Process for Colored Prints

In most processes for the manufacture of a number of colored prints, three color separation negatives are prepared (exceptions: "Kodachrome," "Kodachrome" Professional, "Kodacolor" prints, and "Ansco Printon"). The colored picture or subject is photographed three times: once through a red, then through a green, finally through a blue filter. In the "one-shot" camera, the three negatives are obtained simultaneously. In addition, "Kodachrome" and "Ektachrome" transparencies, which are positives, may be printed onto panchromatic films or plates through Wratten red, green and blue filters, in succession, to provide the same three color-separation negatives.

In the Kodak Dye Transfer Process, each negative is printed on "Matrix' film, exposed through the base, developed, rinsed, and washed in hot water to remove the unexposed, hence still soluble gelatin, and then drying. There is obtained a relief image in gelatin, in which the thickness varies with the intensity of the light. In order to print, the "Matrix" positive is placed in the proper dye bath, where it imbibes an amount of the dye solution propor-

tional to the thickness of the gelatin. The dyed positive is mounted on a blanket and pressed with a rubber roller in a swift motion, onto a coated paper, mordanted to attract the dye. Registry is insured by pressing the dyed "Matrix" film against three fixed anchors in the blanket. The film stemming from the exposure through green is printed in magenta, the one from exposure through red in cyan, and the one from exposure through blue in yellow. An excellent reproduction results which needs only drying. Before soaking in the dye bath, the "Matrix" film is expanded by immersion in hot water. Many other actual steps are omitted in this brief description.

"Technicolor" Moving Picture Film

"Technicolor" moving-picture film is a three-color transparency. The exposure is made in a "one-shot" camera, to produce three color-separation negatives on three light-sensitive films running at equal speeds. The light is divided by a "beam splitter"; one third goes off at an angle, reaches a filter, and forms the green record. The remaining two thirds travel through a blue-sensitive film, then through a red filter to reach finally a red-sensitive film. After exposure, processing is the same as for normal black-and-white photography; three color-separation negatives result: the red, the green, and the blue records. The negatives are printed on "Matrix" film, then developed in a tanning developer, and processed further, to give a positive image in gelatin relief. Each film is colored with a dye which is complementary to the original taking color. Here again, the amount of dye imbibed is proportional to the thickness of the relief film. The dyed films are placed in register and the dye is transferred by contact onto a final film provided with a mordanted gelatin coating; the remaining processing steps are taken and the film is ready for projection. In the final film, the dye substance subtracts the complementary colors from white light, so that the original scene is reproduced on the screen. It is a truly subtractive process. For the accommodation of the sound track, in metallic silver, a silver halide emulsion is provided on the film which is then subjected to suitable exposure and processing.

Lithography

The word "lithography" has come to mean the printing from stone or metal in several colors, partly superimposed to reproduce an original artist's painting; it is also used for a great quantity of monochrome (black and white) work. Metals are used in rotary presses. Either aluminum or zinc sheets are employed; they are used over and over again, but the surface must be suitably grained before application of the printing image. Stones are no longer used, except for small work and special studies. The preparation of the metal plate is largely a photographic process. It is appropriate to discuss lithography in this chapter for another reason: the first utilization of the action of light on chemicals was in lithography (Nièpce), preceding photography proper.

In stone lithography, fine-grained limestones (from Bavaria) are covered by hand drawing, with the lines and areas of a single color. The stones are treated with dilute nitric acid for a brief period, which attacks the uncov-

ered portions, leaving the greased portion slightly raised. The stone is placed in a back-and-forth press, and touched at one end by a water-wet roller, further on by an inked roller (paint); the bare stone is moistened, while only the greased portions take the ink.

For the zinc-plate process, the single colors are selected not by the human eye, but by the camera. The original artist's painting is photographed three times (or more), each time through a filter which blocks off one color, but allows the others to reach the gelatin plate; to make this point and subsequent ones clearer, a yellow flower may be selected. The first picture is taken through a violet filter which stops yellow but allows blues and reds to pass; hence the flower will be represented in the developed and fixed plate by clear glass (1). A positive is now made, through a screen of fine black lines on glass (diamond-shaped openings, with 133 lines to the inch, for example); the positive obtained is in the form of dots, which allow gradations in intensity (2). The yellow flower is represented by a deposit of silver, while the rest of the plate is clear glass. A second negative is made (3), and from it, the final positive image on the zinc plate (4). In the second negative, the yellow flower is again represented by clear glass, so that the positive made from it on the zinc plate receives a flood of light wherever there is yellow in the original painting. By means of the other two filters, corresponding series of plates are prepared, for the final red and blue printings.

A certain amount of hand correction is necessary, and this is done increasingly (a) by local staining with dye solution on continuous tone negative, and (b) by the reduction of areas of dots on halftone positives or negatives.

The zinc plate is coated with a solution of albumen containing ammonium bichromate; the solution is spread evenly by spinning the plate on a turntable. After drying with a small electric fan, the plate, hung vertically, is ready for exposure. It is exposed under negative (3) to the special, movable arc lamp. The size of the zinc plate varies, but is perhaps 4 feet by 3 feet; the negatives are of various sizes, frequently that of a magazine cover. The zinc plate is large enough to accommodate a number of images, sometimes as many as 25 or 30. The location of the several exposures is plotted in advance, and the negative moved to the proper place by means of a vertical and horizontal screw system similar to a microscope.

The albumen-bichromate layer becomes insoluble by the action of the powerful arc light. After the exposure, the metal plate is laid on the table in the dark room, and covered completely with a liquid ink, which may contain, in addition to a black pigment, fats, waxes and resins. Cold water is flushed over the plate, and with the aid of light pressure from a sponge the water removes the unaffected portions, while the affected portions remain and become visible. There remains only a treatment with a solution of chromic acid and phosphoric acid, followed by gum arabic, and the plate is ready for the press.

The zinc plate is mounted on the cylinder of a rotary press and the gum washed off. As the cylinder rotates, one set of rollers moistens the plate while another set presents the ink or paint. The bare zinc takes the water,

while the waxy surface of the image repels it; the ink, on the other hand, is repelled by the wet metal, while it is received and accepted by the image. On being pressed against the smooth rubber blanket covering an identical cylinder, the yellow image is transferred to it, and a moment later, is again transferred (offset) from the blanket to the sheet of paper wrapped around a third cylinder of the same size and turning at the same speed. In another press, a zinc plate for the red will have been set in place, and will print, on the sheet already bearing the yellow portions of the picture, whatever was red in the original painting. In a third press, the blue will be applied. A fourth with gray and a fifth with black are common; the number runs as high as eleven, with a corresponding increase in beauty and also in cost.

Printing from zinc or aluminum plates bearing several images is called multiple printing; the roll makes 3000 to 3600 r.p.h. and for each revolution, a sheet with perhaps 25 images is inked. The modern lithographic press is a precision machine.

In the "deep-etch" process of more recent introduction, the zinc plate is covered with a special gum-containing coating generally colored green and exposed under a positive on glass. After exposure, the unaffected parts are cleared with a zinc chloride solution containing lactic acid. The bare metal is etched, and impregnated with ink: this is the image which will print in the press. The protected parts of the coating are now removed, and the corresponding metal surface desensitized by gum arabic and, for example, nutgall solutions. In the deep-etch plate, the ink, and hence the image, is etched on the metal, just as in the old "transfer" plates, besides being countersunk 0.0001 to 0.0002 inch beneath the plate surface; there is no film of albumen to wear away. The deep-etch process has been deservedly successful.

Of late there has been developed the Kodak Fluorescence Process for photomechanical reproduction, in which images are painted in special fluorescent colors. Photographs through filters of such paintings, illuminated with ultraviolet-containing light, make it possible to employ photographic color correction, and reduce handwork to a minimum.

The production of photographic chemicals in the United States in 1946* was as follows:

	Pounds	Valued per pound at
Hydroquinone	1,941,000	$0.65
p-Hydroxyphenylglycine	10,000	2.50
p-Methylaminophenol sulfate (Metol Rhodol)	563,000	1.92

* U. S. Tariff Commission.

The value of photographic goods is indicated in Table 140.

TABLE 140.—*Value of photographic goods manufactured in the United States in 1947.**

Film	TSFSM	619,142,000	$142,773,000
of which motion picture film, amateur roll film		450,796,000	88,939,000
Photographic (sensitized) paper and cloth			60,079,000
Still picture equipment			94,804,000
Motion-picture equipment except film			91,120,000
Total photographic equipment and supplies			433,807,000

* Census of Manufactures, Dept. of Commerce.

Blueprints. The light-sensitive paper used for blueprints consists of white paper coated with a solution of ferric ammonium citrate and potassium ferricyanide; the coating is done automatically, in rooms with subdued light. An India ink tracing on cloth supported by a coat of pyroxylin is placed between the sensitized paper and the source of light; the black lines protect the coating, but elsewhere the iron of the citrate is reduced (from ferric to ferrous). On immersion in water, the unaffected mixture dissolves while the reduced iron forms the insoluble blue ferro-ferricyanide[5]; the fixing agent is merely water. The result is a design of white lines on a blue field.

In the *Osalid process*, a positive on the tracing cloth produces a positive with deep purple lines on a white background. Osalid paper is coated with a diazo anhydride; on exposure, a faint yellow image (negative) is produced. It is developed in ammonia vapor, only the protected portions reacting.

Of increasing importance is the process known as photostating, in which the page of a book, print, or picture is reproduced as a paper negative by the reflection of strong light; the negative may then in turn be illuminated, and made to produce a positive. The paper used is a silver bromide paper. No plate or film is necessary.

Other Patents

U. S. Patent 2,005,837, manufacture of photographic emulsions; 1,991,136, photographic emulsion; 1,787,564, manufacture of fire-proof photographic films; 1,890,026 and 1,890,490, apparatus for propelling long strips of films, such as motion picture films, through a liquid bath; 1,815,513, manufacture of films from an aqueous cellulose solution; 1,889,818, apparatus for developing photographic films; 1,860,059, apparatus for developing roll films; 1,742,814, machine for assembling photographic films; 1,836,023, lithographic printing machines; 1,820,593, lithographic plate and process of preparation. U. S. Pat. 2,425,403, a new fluogermanate glass, containing germanium oxide, titanium oxide and sodium fluoride for wide-angle camera lenses and microscope objectives.

Reading References

"Data book on color photography with Kodachrome and Kodacolor film," Eastman Kodak Company, Rochester, N. Y., 1945.

"The history of color photography," Joseph S. Friedman, Boston, American Photographic Publishing Co., 1944.

"History of three-color photography," E. J. Wall, Boston, American Photographic Publishing Co., 1925.

"Photography," C. E. K. Mees, New York, Macmillan Co., 1945.

"Ansco color film," in Sept.-Oct. 1943 issue of *The Ansconian*, Binghamton, N. Y.

"Photographic sensitizing dyes," L. E. Wise and E. Q. Adams, *Ind. Eng. Chem.*, 10, 801 (1918).

"The reactions of photographic materials to light," S. E. Sheppard, *Ind. Eng. Chem.*, 22, 555 (1930).

"Electrolysis of silver-bearing thiosulfate solutions," K. Hickman, W. Weyerts, and O. E. Goehler, *Ind. Eng. Chem.*, 25, 202 (1933).

"The chemistry of photography," articles by S. E. Sheppard, *J. Chem. Ed.*, 4, 465 and 749 (1927).

"The science of photography," C. E. Kenneth Mees, *Sigma Xi Quarterly*, 19, March (1931).

"Photo Progress in 1948," Glenn E. Matthews, Photographic Society of America Journal, Jan. 1949, p. 12.

Article by James E. Henry, in Photogrammetric Engineering, Mch. 1948, p. 111.

[5] Ferri-ferricyanide is not blue, but brown, and is soluble in water.

Chemical fertilizers play an important rôle in increasing the crops of grains and cotton. In another way, chemical science has made itself almost indispensable to the agriculturist, in the killing of insects which render the fruit wormy or destroy the foliage, and in the control of fungi which spot the fruit and destroy the trees or vines. Such crops as the potato, tobacco, and cotton are all subject to pests which are successfully fought by means of chemical poisons.

Chapter 38

Insecticides and Fungicides

The application of chemical substances below the soil provides the plant with extra food which permits better growth resulting in a greater yield per acre; but above the soil, the plant also stands in need of the products of chemical science, in the form of insect killers (insecticides) and fungus destroyers (fungicides). The apple tree alone, for example, is subject to the following insect pests: the codling moth, the San José scale, the aphis, red bug, apple and thorn skeletonizer, bud moth, apple maggot, gipsy moth, canker worm, and nine more.[1] In addition it is subject to fungous diseases such as the apple scab, cedar rust, and several others. The proper choice of chemicals is determined by experiments performed at State and Federal experiment stations, and the knowledge so obtained is offered free to the agriculturist. The method of application is by spraying a suspension of the chosen materials in water, or by "dusting" the powdered dry material; in general spraying is better, and more widely practiced. The system of protecting crops in this way has become of great importance and wide application, so much so that unsprayed fruit is essentially unsalable. The most important substances employed are lead and calcium arsenates, sulfur, lime-sulfur, Bordeaux mixture, kerosine and other emulsions, and powdered poisonous plants. These older, standard agents have been supplemented by a number of more recently developed materials, synthetic organic compounds, among which are DDT and hexachlorocyclohexane. For certain dieases such as the fire blight, a bacterial disease (apple tree), the remedy is to cut off the affected branches and twigs in the wintertime, and to disinfect the cuts with a solution of mercury bichloride ($HgCl_2$). The destructive insect pests are held in check also by birds, toads, beetles, and parasitic insects; other means of protection are banding the tree trunks with sticky materials to prevent the ascent of caterpillars and wingless moths, band traps, and local application of the fire torch.

Insecticides

The agricultural insecticides may be divided into three classes: (1) the stomach poisons, for insects which eat the foliage; these include arsenate of lead, arsenate of calcium, hellebore, and paris green; (2) the contact insecticides, effective against insects which do not eat the foliage, the boring

[1] "Injurious insect.pests and fungous diseases," *N. Y. State Dept. Farms and Markets Cir.* No. 292, 3-10 (1925).

insects; to this group belong lime-sulfur, nicotine dust, and kerosine emulsions; (3) the fumigants, used against borers which are not reached by sprays, and for the protection of grain stored in warehouses; some of the substances in this class are carbon disulfide, hydrocyanic acid, ethyl acetate-carbon tetrachloride mixture. The divisions are not strict, for one substance may serve in two classes.

The Stomach Poisons. The production of lead arsenate, calcium arsenate and paris green depends upon arsenic, usually arsenic trioxide or white arsenic, and a discussion of their manufacture will of necessity include a few words about the availability of arsenic trioxide.

White arsenic, As_2O_3, is a by-product of the smelting of copper and lead; it passes out with the fire gases and may be collected in settling chambers, in bag filters, or in the Cottrell electrical [2] precipitator. The removal of the arsenic dust is obligatory in many states, so that a certain source for white arsenic is assured; it is, however, also obtained by roasting arsenic sulfide ore and other ores, in which operations it is the primary product. When the copper smelters work to capacity, the Anaconda smelter (Montana) alone can supply 10,000 tons annually from its Cottrell precipitator.[3]

In 1946, the production of white arsenic was abnormally low, because of shutdowns due to strikes; there were produced 8,981 tons of crude, 1,230 tons of refined white arsenic, a total of 10,211 tons, about one-third of the usual production. Importations exceeded production in 1946. The consumption is due in large part (87 per cent) to the manufacture of arsenical insecticides, to a lesser extent to the manufacture of plate glass (3 per cent).

White arsenic heated with Chile saltpeter gives sodium arsenate, Na_2HAsO_4, and this in solution may be used to make the lead and calcium arsenates. Other ways to change the white arsenic, As_2O_3, to arsenic acid, H_3AsO_4, are by means of chlorine in presence of water,[4] followed by sufficient concentration to drive off the hydrochloric acid formed in the reaction, and by heating with nitric acid and evaporating to a syrup. Lead arsenate is made by suspending litharge, PbO, in a solution of arsenic acid in the presence of nitric acid or acetic acid [5]; an improvement is to use sublimed lead oxide (yellow) (PbO) made into a cream with water, and add to this the solution of arsenic acid.[6] The reaction takes place at room temperature; the lead arsenate precipitates and is filter-pressed and sold as a paste, or, as is becoming the general custom, is dried and shipped as a powder.

The precipitate does not settle very well; indeed it is essential that it should remain in suspension for long periods when made up for spraying; a proposal was made to avoid any kind of washing by adding magnesium hydroxide, $Mg(OH)_2$, after the lead oxide had reacted, to bind the remaining arsenic acid or arsenate of sodium.[7] The resulting product is a mixture

[2] Chapter 43.
[3] *U. S. Tariff Information Survey,* FL6, U. S. Tariff Commission, Washington, D. C., 1921, p. 11.
[4] U. S. Patent 1,169,114.
[5] U. S. Patent 892,603.
[6] U. S. Patent 1,228,516.
[7] U. S. Patent 1,417,232.

of magnesium and lead arsenates, $MgHAsO_4$ and $PbHAsO_4$, which is said to be an excellent insecticide.

An excess of lead is always provided, for soluble arsenic beyond a certain figure (1 per cent As_2O_3) is prohibited by the Federal Insecticide Act of 1910. When lead nitrate is treated with arsenic acid, the acid lead arsenate, $PbHAsO_4$ precipitates and remains in suspension even better than the neutral salt, contains more arsenic, and is quicker in action on the insect. When lead acetate is used instead of the nitrate, the neutral lead arsenate, $Pb_3(AsO_4)_2$, is formed; this is less injurious to foliage, and remains in suspension very well; it is used for peach and plum trees. In the process using lead oxide, the kind of lead arsenate formed is determined by the amount of lead oxide used to a given amount of arsenic acid. Both the acid and the neutral lead arsenates are insoluble in water.

$$PbO+H_3AsO_4 \rightarrow PbHAsO_4+H_2O;\ 3PbO+2H_3AsO_4 \rightarrow Pb_3(AsO_4)_2+3H_2O.$$

Lead arsenate may also be manufactured in the dry way, by burning powdered lead sulfide or metallic lead and white arsenic in a blast of hydrocarbon fuel; the oxidation and combination occur in the high heat of the burning fuel. The lead arsenate formed is collected in settling chambers and bag filters.[8]

Calcium arsenate, also a white powder or paste, is made by running a solution of calcium chloride, $CaCl_2$, into an alkaline solution of sodium arsenate, Na_2HAsO_4:

$$3CaCl_2+2Na_2HAsO_4 \rightarrow Ca_3(AsO_4)_2+4NaCl+2HCl;$$

the hydrochloric acid is removed by the alkali in the sodium arsenate solution. The calcium arsenate is insoluble; it precipitates and is filter-pressed and shipped as a paste or dried to a powder.

Calcium arsenate may be substituted for lead arsenate, except in treating trees with tender foliage; it is more injurious than the lead arsenate; it is less adhesive, but this may be remedied by using it in conjunction with Bordeaux mixture, or with lime. The great advantage of calcium arsenate over lead arsenate is its lower price (11 cents a pound against 32 cents) which has permitted among other things its use in cotton fields for the destruction of the dreaded boll weevil. Calcium arsenate has been found a superior insecticide for this pest, and the general method of application is as a dust, without dilution.[9] But even at 11 cents a pound, calcium arsenate is too dear for general use in cotton fields against the boll weevil. Dilution would not do, but a method of preparation has been found by means of which an inert kernel of calcium carbonate is coated with calcium arsenate, the resulting powder being as effective as pure calcium arsenate. Mixtures

[8] U. S. Patent 1,175,565.

[9] "The principles of insect control," Wardle and Buckle, Manchester, University Press, 1923, p. 90. The cotton fields are dusted from airplanes as well as by means of tractor or mule-drawn spreaders. A service in Stuttgart, Arkansas, for example, operates 18 planes (called ships), taking contracts anywhere in the United States. There is claimed for the airplane distribution method a greater evenness, besides rapidity; 300 to 400 acres per hour are dusted, whereas with the ground methods, 50 acres per day is the average man's work. The ship flies 3 feet above the top of the plants; if necessary, even closer, such as 6 inches (wind). This is exceedingly dangerous work for the plane operator.

of precipitated chalk and white arsenic are heated with excess air at 650° C.; the arsenic is changed to the pentavalent form, as normal tricalcium arsenate. It has been established that this material, with only 24 per cent As_2O_5, is as effective against the boll weevil as ordinary calcium arsenate, with 40 per cent As_2O_5.

The production of lead arsenate and calcium arsenate in 1946 was the lowest in many years; for lead arsenate, it stood at 27,907 tons, for calcium arsenate at 17,630 tons. The high figure in recent years for lead arsenate was 45,352 tons, in 1944, and for calcium arsenate 38,898 tons, in 1942.

FIGURE 256.—The full-size sprayer assembly consists of a tractor, and the spray tank with a small pump for the liquid and a blower. Pump and blower are operated by a separate gasoline engine. Dry dust is applied with very similar apparatus. (Apple orchard, Cobblestone Fruit Farm, Sodus, N. Y.)

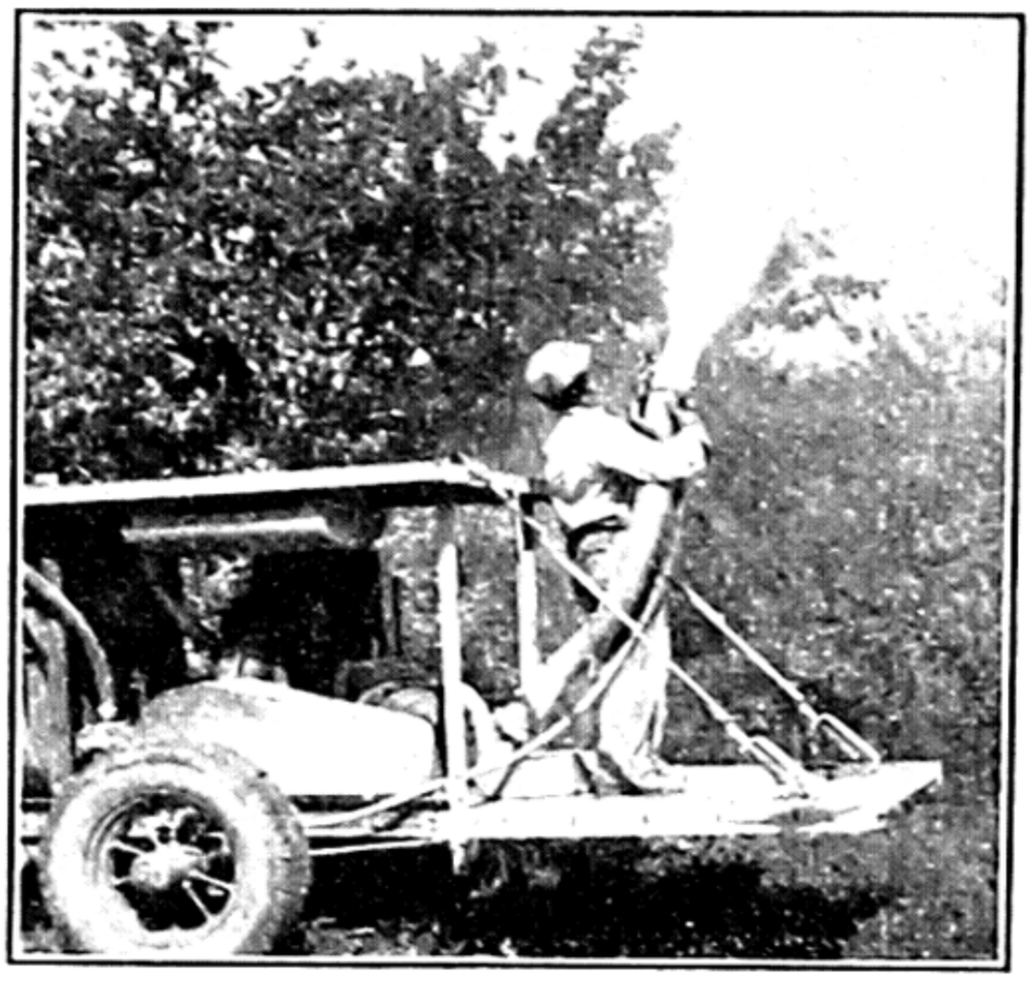


FIGURE 257.—The lime-sulfur solution is atomized in the nozzle and the rich mist directed into the tree. Pump for the liquid is at left; the blower is just behind the operator. (Spraying McIntosh apple trees, Sodus, N. Y.)

In spray form, the proportions recommended for both lead arsenate and calcium arsenate are 1 pound of the powder to 50 gallons of water (about 0.25 per cent). The method of spraying trees in orchards requires two operators; a gasoline-driven pump and a tank are placed on a flat-topped wagon; one man guides the horses or the tractor, the other directs the spray.

Paris green is used in appreciable quantities, though smaller than those of the preceding two arsenicals. Many farmers consider paris green the best remedy against the potato bug. The method of manufacture is to add a solution of copper acetate to a solution of arsenious acid, H_3AsO_3; there is precipitated a copper acetoarsenite of indefinite composition. This is filter-pressed and dried. Paris green has a higher tolerance for water-soluble arsenic than lead arsenate; it must not exceed $3\frac{1}{2}$ per cent As_2O_3. The production in 1945 was 1,950 tons.

The Contact Insecticides. The contact insecticides are effective against the boring insects which have soft bodies, such as scale insects, plant lice,

pear thrip, red bug, red spider, and others. By means of these chemicals, the insects are poisoned, paralyzed, or killed, either by covering the skin with a film of oil which closes the breathing pores, or by absorption through the skin. Lime-sulfur, nicotine, soap solutions, kerosine, and oil emulsions are the important members of the first group; pyrethrum, rotenone, DDT of the second.

Lime-sulfur is used both in solution, as a spray, and in the dry powder form, as a dust. It is manufactured by boiling sulfur in milk of lime, with the formation of calcium polysulfide and small amounts of a number of sulfur compounds of no importance. The solution is yellowish-brown; after filter-pressing or decanting the clear liquor, it is concentrated to 32° Bé. cold, when it contains about 24 per cent of sulfur in solution. This solution is shipped in tight oak barrels, and is diluted with 8 parts of water for the San José scale, 16 parts for the peach leaf curl, 42 parts for apple tree spray, and 54 parts for pear and cherry trees.[10] There is also in wide use a home-made lime-sulfur solution, which has the same composition and effectiveness as the commercial material. Lime-sulfur is also sold in the dry form, which may be applied as a dust. The annual production of lime-sulfur solution is in the neighborhood of 10 million gallons.

Nicotine in the form of nicotine sulfate is made from refuse tobacco and is sold as a 40 per cent solution. This is diluted so that the spraying liquor contains not less than 0.06 per cent nicotine; it is advisable to dilute in a soap solution, which acts as a spreader, containing 2 pounds of soap to 50 gallons of water. A satisfactory nicotine extract may also be home-made, by steeping stems and sweepings of dried tobacco in water at ordinary temperature. If refuse tobacco is purchased, the cost is reduced, as the extracted material is a good fertilizer. The strength of the extract is fixed by using definite weights of tobacco, and consulting the table furnished by the United States Department of Agriculture.[11] Such home-made extracts contain the nicotine in the form of the free base; the commercial, concentrated extract is the sulfate of nicotine, because the free base is volatile and would be lost during concentration, whereas the sulfate is fixed.

Nicotine powder is made by pulverizing stems, and may contain very little nicotine. The strong extract may be applied in the form of a dust by mixing it with gypsum, kaolin, or hydrated lime, or a mixture of these; the choice of the added solid has a definite influence upon the effectiveness of the dust.

Soap solutions are usually fish-oil soaps, containing 1 pound of soap to 4 gallons of water or more; the strength depends on the kind of insect to be destroyed. Fish-oil solutions are efficient against plant lice. The soap solution is frequently used with nicotine solutions, arsenate of lead and Bordeaux mixture. The soap may be purchased, and may be a potassium or sodium soap, preferably the former; it may be home-made from fish oil and lye; in either case, the soap retains a strong fish-like odor.[12]

[10] "Injurious Insect Pests and Fungous Diseases," reference 1, p. 59.

[11] "Insecticides and equipment for controlling insects on fruits and vegetables," N. F. Howard, C. A. Weigel, C. M. Smith and L. F. Steiner, Dept. Agr., Miscellaneous Publication 526, 1945, pp. 23-26.

[12] Ref. 11, p. 32.

Kerosine, crude-oil, and lately lubricating-oil emulsions have been used with success. A kerosene-oil emulsion may be made as follows: one-half pound of fish-oil soap is dissolved in 1 gallon of water, and 2 gallons of kerosine added to the hot solution; by pumping it back and forth, or by violent agitation, a creamy emulsion forms, which does not separate on cooling. For use on dormant trees, the dilution is 1 part to 7 of water.[13] Other emulsions are made in a similar way.

Miscible oil emulsions are made by mixing an emulsifying solution containing fish-oil soap, carbolic acid and kerosene, with the "miscible oils," paraffin oil (28° Bé.) and rosin oil.[14]

Pyrethrum and rotenone, either in powder form or the extract, are widely used as horticultural and household insecticides. Pyrethrum is obtained from the flower heads of *Chrysanthemum cinerariaefolium* and two other species, cultivated and harvested in Dalmatia, before World War I, in Japan later, and now mainly in Kenya, British East Africa and in the Belgian Congo.

The production of pyrethrum in Kenya in 1946 was 6,370 long tons; 4,520 long tons in 1947, and about 3,000 tons in 1948, mostly exported to the United States.

Pyrethrum has the unique property of quickly immobilizing the insect on contact; it is for that reason always included in sprays for household pests and in aerosols, supplementing other active ingredients such as DDT. The extract of pyrethrum contains the pyrethrins, and is used more generally at present than the pyrethrum powder, formerly widely employed as "insect powder."

Rotenone is the active principle in *Derris elliptica*, commonly called tuba, and cultivated in British Malaya and Indonesia. The root may be powdered, and diluted with talc to 1 per cent; or it may be extracted.[15]

Synthetic Organic Insecticides. The insecticidal properties of DDT, discovered near the beginning of World War II, and its unobjectionable, faint odor, led to its widespread beneficient use during the war period, helped along still further by a shortage of pyrethrum and rotenone at the time. DDT is a white solid with a weak, fruity odor; the initials stand for dichlorodiphenyltrichloroethane, more precisely 2,2 bis- (*p*-chlorophenyl)-1,1,1-trichlorethane. A method for its manufacture in practice, both for batch and continuous operations, is the reaction between chloral (30 parts) and chlorobenzene (60 parts), in the presence of sulfuric acid or oleum:

$$\underset{\textit{chloral}}{CCl_3 \cdot CHO} + \underset{\textit{chlorobenzene}}{2C_6H_5Cl} \rightarrow \underset{\textit{DDT}}{(Cl \cdot C_6H_5)_2CH \cdot CCl_3} + H_2O$$

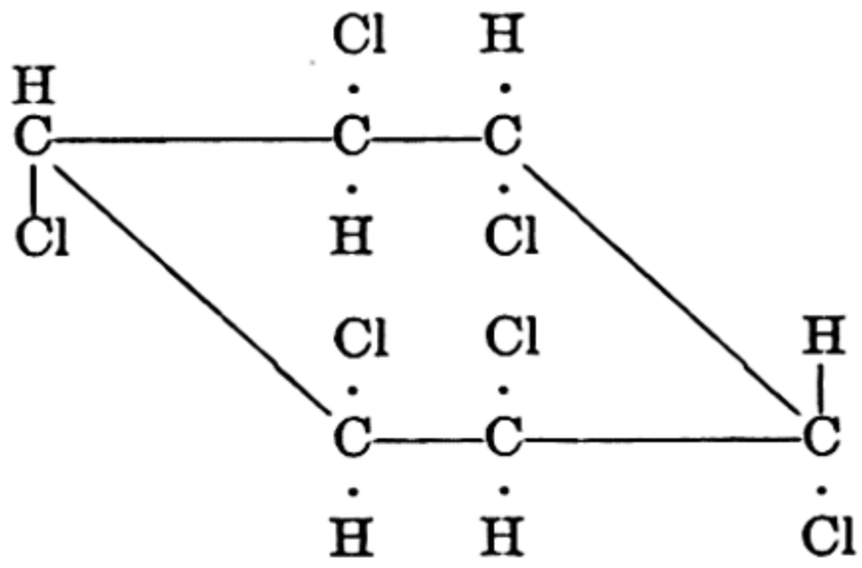
After reaction, the mix is poured into water, and the new product separates out. Other chlorinated ethane compounds are formed; the technical DDT therefore contains only about 70 per cent of the pure substance. It may be dissolved in organic solvents, and the solution may be applied as a spray against the housefly, mosquito, and other pests, or in the form of emulsions with water. DDT is highly favored in aerosol bombs, usually combined

[13] "Injurious Insect Pests, etc.," reference 1, p. 55.
[14] Ref. 11, pp. 20 and 37.
[15] "Chemistry of insecticides, fungicides and herbicides," 2nd ed., p. 159, Donald E. H. Frear, New York, D. Van Nostrand Co., Inc., 1948.

with pyrethrum, and with sesame oil, soybean or peanut oil as a synergist. The dry powder mixed with inert solids such as bentonite and gypsum (but not lime) is applied as a dust. To the diluted powder a wetting agent may be added to form a water-dispersible powder; this is the favorite method in orchards. The solution is made up with water, and applied as a spray. DDT sprays are effective against the apple worm.

DDT is both an insecticide, a pesticide, and a larvicide. In the war period, thousands of civilians in the countries at war were safeguarded from typhus by dusting, in order to kill the fever-bearing louse. Troops in Europe were provided with DDT -impregnated shirts for protection against lice. Poured on stagnant waters, it kills mosquito larvae, reducing or destroying completely the malaria-bearing insect. New applications of DDT are reported at frequent intervals. The production of DDT in 1948 was 18,346,727 pounds, less than the 1947 production, and not half the 1946 production.

Hexachlorocyclohexane ($C_6H_6Cl_6$, more precisely 1,2,3,4,5,6-hexachlorocyclohexane) has 16 stereoisomers, of which only one, designated as gamma, has high toxic properties. Hexachlorocyclohexane is made by chlorinating benzene under the influence of short-wave light; in the product of the reaction, the gamma isomer exists to the extent of 10 to 14 per cent. The technical product is used as such, without isolating the active isomer. Its configuration [16] is:



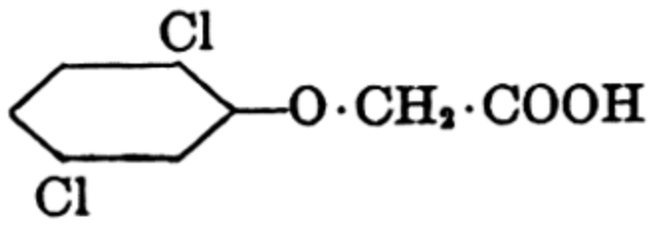
Gamma isomer of hexachlorocyclohexane

Its melting point is 112.5° C., much lower than that of any of the other four more frequently occurring isomers.[16]

Since hexachlorocyclohexane has a persistent odor, it is not favored as an agricultural insecticide on food crops; it has been applied with success to such crops as cotton. It has been used, in the low concentrations which suffice, against the grain weevil. In its many other applications, it does not compete with DDT, but rather supplements it. The production of hexachlorocyclohexane in the United States in 1948 came to 15,764,519 pounds, with a gamma-isomer content of 2,112,209 pounds.

Chlordane, another of the newer organic insecticides, is an octa-chlor derivative of tetrahydroindane.[16]

The ammonium salt of 2,4-D, that is, 2,4-dichlorophenoxyacetic acid, or



[16] "Chemistry of insecticides, fungicides and herbicides," 2nd ed., pp. 82, 83, Donald E. H. Frear, New York, D. Van Nostrand Co., Inc., 1948.

is a selective herbicide. It will destroy broad-leaved weeds in a wheat field, for example. A production figure for 2,4-D was not reported prior to September, 1948; in the last four months of that year, however, it was reported to have reached a total of 8,433,515 pounds in a third of a year.

In dilute solutions, 2,4-D is a growth regulator; in more concentrated solutions, it is a selective weed killer. Other growth regulators are α-naphthalene acetic acid, which has been used in dust form, to prevent premature fruit drop on apples. Colchicine promotes vigorous growth by inducing polyploidy.

Ammonium sulfamate, $NH_2 \cdot SO_3 \cdot NH_4$, in water solution destroys poison ivy.

Aerosols. Aerosols are air suspensions of solids (or liquids) in a fine state of subdivision which lies in the colloidal range. There are a number of different kinds of aerosols, produced in different ways. One of the best known and most widely used is the liquefied gas aerosol, which consists of a mixture of a liquefied gas (such as "Freon" 12) and a concentrated oil solution of insecticide ingredients which is completely soluble in it. The mixture is contained in a portable bomb provided with a valve. Upon release of the valve, a part of the compressed liquid solution escapes; the liquefied gas vaporizes instantaneously and leaves in suspension the less volatile liquid and the solid insecticide (such as DDT). On closing the valve, the remaining charge is preserved until required. The liquefied gas is the propellent for the insecticide (the toxicant). The finely divided toxicant is effective against mosquitoes, and any insect present in a tent or other enclosed place. Generally the liquefied gas is 80 to 90 per cent, the insecticide solution 20 to 10 per cent by weight of the bomb charge. Aerosols for insect control for humans may contain dimethyl phthalate, an effective repellent.

TABLE 141.—*Analysis of charge in household aerosol bomb.*
(Examples)

High pressure	
DDT (purified)	3.0%
Pyrethrine	0.4
Hydrocarbon oil	11.6
"Freon" 12	80.0

Low pressure	
DDT	2.00%
Pyrethrine	.20
Butyl "Carbitol"	1.28
Other similar compounds	.32
Petroleum distillate	11.20
Inert propellent	85.00

Low pressure	
DDT	2.00 %
Pyrethrine	.20
Sesame oil extratives	
Sesamin	.166
other extr.	.834
Petroleum distillate	11.80
Propellent	85.00

Insecticides in Vapor and Gas Form; Fumigants. Stored wheat and other grains are subject to insect pests which are readily destroyed by pouring carbon disulfide on the grain and closing all outlets; such fumigations are practicable only when the material is contained in a building which can be closed hermetically during treatment. Carbon disulfide and air mixtures are explosive; to avoid this danger, a new fumigant has been developed, a mixture of ethyl acetate and carbon tetrachloride which is non-explosive, vaporizes almost as readily, and is nearly as efficient.

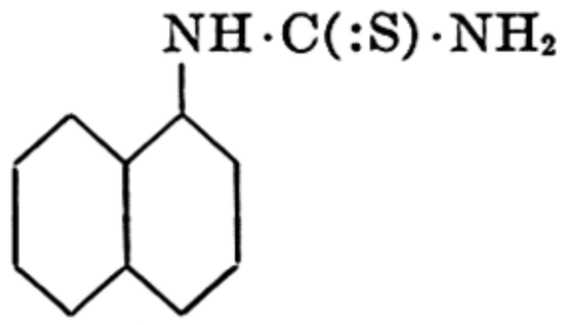
Hydrocyanic acid, HCN, is an excellent fumigant, and although a deadly poison to man, may be handled safely. A dish containing the proper amount of sodium cyanide is placed underneath a bottle containing sulfuric acid, which can be upset from near the door by an arrangement of strings and small pulleys. As the operator is about to step out, he pulls the string and closes the door. This gas is applied to citrus trees in California, by placing over the tree a cotton duck bag which reaches to the ground; the gas is generated by acid on sodium cyanide and destroys the insects without hurting the tree. Calcium cyanide is also used.

"Carboxide" is the trade mark for a mixture of 1 part ethylene oxide and 9 parts carbon dioxide, a safe and effective fumigant; it is non-inflammable and non-explosive. It is obtainable compressed to a liquid in steel cylinder; the material issues from the cylinder in a fine spray or mist which vaporizes immediately.

Soil fumigants are employed in order to destroy the nematodes which can ruin a potato crop, sugar beet and other crops by entering, and tunneling in the roots and tubers. The more expensive chloropicrin has been succeeded since 1945 by D D, a liquid mixture of dichloropropane and dichloropropene (also "Dowfume" M). Two other nematocides are ethylene dibromide and methyl bromide, each of which is adapted to specific tasks.

The peach borer works near the ground and cannot be reached by sprays or dusts; para-dichlorobenzene, a solid, placed in a small trench around the base of the tree, destroys it.

Among the newer *rodenticides*, there should be mentioned "Antu" (alpha-naphthyl thiourea) a rat poison. It has very little effect on humans.



α-Naphthyl thiourea

Barium carbonate is a rat poison, used considerably in past years; it is harmless to dogs. Sodium fluoroacetate has given good results, but it is dangerous to humans, so that it can be used only by experts.

Fungicides

The fungous diseases which attack the fruit-trees, vines, and farm crops are perhaps more serious even than the insect pests, because once the fungus has grown, it is so tough that it resists chemicals; it is only while the spores are young and tender that they can be destroyed with surety. The work against fungous diseases thus takes on the aspect of prevention rather than cure; in keeping with this policy, nursery stocks and seeds are fumigated and dipped before sale. The dust called "Semesan" (Dupont), for example, containing 35 per cent hydroxymercuriphenol, applied to the seeds, destroys fungi (which include molds and bacteria).

Some of the fungous diseases are mildews, apple and other scabs, rust, leaf spot, brown rot of plum and peach, and bark cankers. The important

fungicides are sulfur, Bordeaux mixture, lime-sulfur, already listed as a contact insecticide, formaldehyde, corrosive sublimate ($HgCl_2$), and a number of organo-mercuric compounds.

Sulfur, in the form of a fine powder under the names of dusting sulfur (99 per cent S), sulfo-dust, dry mix (61 per cent S) and others; is applied mainly as a dust, in a few cases as a suspension in water, or better, soap solution. It is estimated that in Europe over 100,000 tons of powdered sulfur or flowers of sulfur (sublimed) are used every year against the microscopic fungus *oidium*, which causes the grape vine leaf to dry.

FIGURE 258.—Melted sulfur brought to the surface from the subterranean deposit being discharged into a sulfur vat, at New Gulf, Texas. The discharge pieces are the latest type; they spread the flow which formerly was concentrated in a stream. (Courtesy of the Texas Gulf Sulfur Company, New York, N. Y.)

Sources of Sulfur. The main sources of sulfur are Sicily and the Louisiana and Texas deposits; sulfur occurs in many other places, however, such as Japan, Mexico, and in the state of Wyoming. In Sicily, the sulfur occurs mixed with marl and gypsum; it is purified by heating and draining or running off the liquid sulfur; the fuel is sulfur. In the coastal plain of the Gulf of Mexico, a strip of land 225 miles wide is sulfur-bearing; it lies partly in Louisiana, and partly in Texas. The sulfur lies at depths of 600 to 1100 feet, and the deposits average 125 feet. It is lifted to the surface from deposits between 600 and 2000 feet deep by means of the Frasch process.[17] The sulfur pocket must be covered by a fairly thick and tight cap, for the superheated water must be kept under 100 pounds gauge pressure, in order to retain for it the temperature of 340° F. (171° C.). The heated water is forced down 6-inch casings into the deposit; the melted sulfur [melting point 112.8° C. (235°F.)] is forced upward through a 3-inch casing strung inside the outer 6-inch one. A 1-inch pipe inside the 3-inch one carries compressed air (500 pounds)

[17] "The manufacture of sulfuric acid in the United States," Wells and Fogg, *Dept. Interior Bull.* No. 184, p. 27; see also *Ind. Eng. Chem.*, 4, 136, 140, 143 (1912).

to the liquefied sulfur and, mixing with it, divides it into gullets separated by the air, which makes a column easier to lift. Not only must sulfur be located, but other conditions must be met before the mining of a given deposit can become a reality. For the production of 1000 tons per day, 2 to 3 million gallons of water are required, a 4000-horsepower boiler plant, fuel, pipe lines and bins for receiving the liquid sulfur, and the possible necessity of disposing of "bleed" water from non-producing wells in the same dome.[18] Continuous operation in the Frasch process is essential, for, if interrupted, the liquefied sulfur in the formation congeals and "freezes" the pipes in each hole.

The main uses of sulfur are as a fungicide, for making lime-sulfur, for the sulfite pulp process in paper-making, for manufacturing sulfuric acid (supplementing pyrite), for vulcanizing rubber, and for the manufacture of carbon disulfide.

The production of sulfur as brimstone in the United States, mainly from Texas and Louisiana, is shown in Table 142. By-product sulfur is presented in Chapter 14.

In countries without sulfur deposits, the manufacture of elemental sulfur is the goal of numerous efforts, the most successful of which is the one in Norway, where the Orkla Metal Co. manufactures brimstone sulfur from

TABLE 142.—*Production of sulfur; exports (1946).**

	long tons
Sulfur produced from mines, total U. S.	3,859,642
of which from Texas	2,975,472
of which from Louisiana	884,170
Shipments of crude sulfur, for domestic consumption	2,939,140
Shipments for export	1,189,072

* "Minerals Yearbook."

cupri-ferrous pyrites.[19] The pyrites are smelted with coke, quartz and limestone; a large part of the iron forms a slag, while the copper and other metals combine with some sulfur to form a matte, which is then suitably worked up separately. The gases from the furnace contain gaseous sulfur, sulfurous acid and carbon disulfide. With the aid of suitable catalysts, these various gaseous compounds are made to react, forming CO_2 and free sulfur. The latter is solidified by condensation and subsequently treated by a nodulizing process, which eliminates dust and produces a granular product. The sulfur is of high purity, entirely free from bituminous matter, and seldom contains more than 0.01 per cent ash. A recovery of 85 to 90 per cent of the sulfur and copper content is obtained. Heat recovered in cooling the furnace gases and condensation of the sulfur supplies enough steam to run the entire plant.

Elemental sulfur is made at Trail, B. C., from sulfur dioxide, by passing the 100 per cent gas through a bed of incandescent coke. There pass out of the reactor sulfur vapors and oxide of carbon. The former is condensed by cooling, remelted, and cast into bars. The strong sulfur gas is obtained by

[18] J. H. Pollard, *Chem. Met. Eng.*, 39, 394 (1932).
[19] "Mineral Resources," 1932-1933, p. 685.

absorbing roaster gas (8 per cent) in ammonium sulfite solution, and subsequently treating the latter with sulfuric acid.[20]

Bordeaux mixture is probably the most important fungicide used in the United States; it may be purchased in the form of a powder and made up with water, or it may be home-made. It consists of copper sulfate and lime,

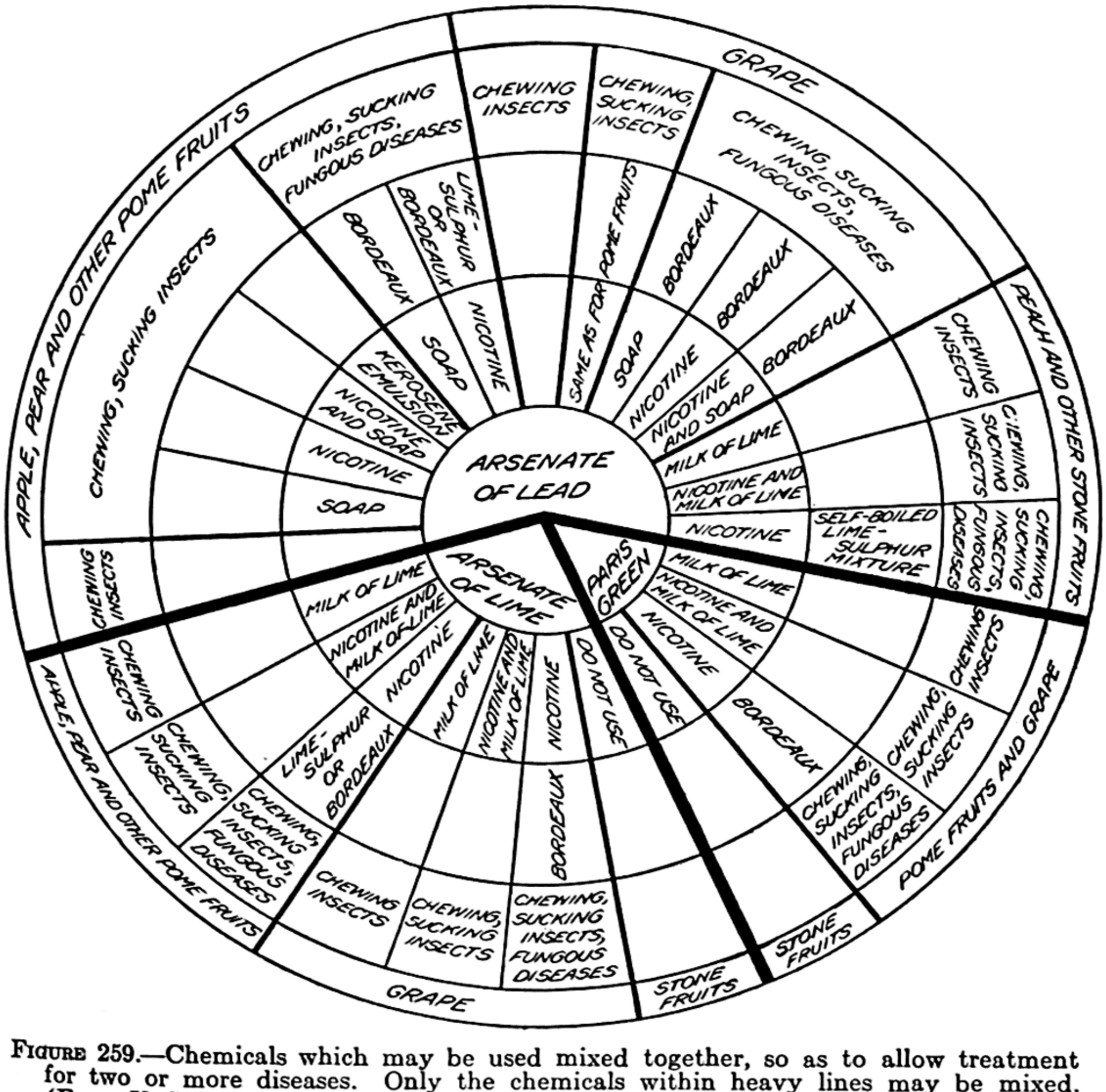


FIGURE 259.—Chemicals which may be used mixed together, so as to allow treatment for two or more diseases. Only the chemicals within heavy lines may be mixed. (From *U. S. Dept. Agr., Farmers' Bull.* No. 908.) A more recent compatibility chart has appeared in the *American Fruit Grower* for February 1949.

and for the home-made spray, ready to apply to the crops, the proportions are as follows:[21] 4 pounds of copper sulfate $CuSO_4 \cdot 5H_2O$, called bluestone, are dissolved in 25 gallons of water; 4 pounds of fresh stone lime, or quicklime (CaO), are dissolved in 25 gallons of water, and the two solutions are mixed, in the spray tank itself, for example. The concentration is correct for

[20] *Chem. Met. Eng.*, 45, 483 (1938).
[21] Ref. 11, pp. 6-8.

summer spraying; a little less bluestone is taken for spring spraying. This mixture gives a bluish deposit, which is very noticeable on the green leaves.[22]

Formaldehyde solutions are used to prevent potato scab, oat smut, the stinking smut of wheat, and onion smut. The method for potatoes is to place the seed potatoes in a solution containing 1 pint of 40 per cent formaldehyde solution (CHOH) in 30 gallons of water, for two hours. The oats may be spread on the floor and the solution poured on them. Other uses and the method of manufacture of formaldehyde will be found in Chapter 35.

The sodium, zinc and iron salts of dimethyldithiocarbamic acid [$(CH_3)_2 \cdot N \cdot CSSH$] are fungicides with specific applications. They were produced to the extent of 3,991,000 pounds in 1947, and valued at $0.59 a pound.

The relative importance of the several more important insecticides, fungicides, fumigants, and allied substances is indicated in the following tabulation:

TABLE 142a.—*Insecticides, fungicides, fumigants and related economic poisons, for 1944. Estimated agricultural consumption.*

(Agricultural Statistics 1945)

	Pounds		Pounds
Lime	435,000,000	Dinitro compounds	4,000,000
Petroleum oils	250,000,000	Phenothiazine	3,500,000
Sulfur (incl. lime-sulfur)	200,000,000	Rotenone	3,500,000
Copper chemicals	103,700,000	Naphthalene, crude	3,000,000
Lead arsenate	85,595,000	Pine oil	2,000,000
Calcium arsenate	36,059,000	Nicotine	1,197,000
Talc	24,000,000	Paris green	1,875,000
Cryolite	15,500,000	Formaldehyde	1,750,000
Pyrophillite	14,000,000	Calcium cyanide	1,500,000
Zinc sulfate	8,900,000	Chloropicrin	750,000
Vegetable oils	8,000,000	Seed disinfectants	600,000
Thiocyanates	6,000,000	Methyl bromide	530,000
Carbon tetrachloride	6,000,000	Pyrethrum	520,000
Ethylene dichloride	6,000,000	Dichloroethylether	500,000
Carbon disulfide	5,000,000	DD mixture	400,000
Sodium fluoride	4,000,000		

Synthetic Insecticides

(From Tariff Commission Report for 1947)

Insecticides, synthetic, total	66,058,000	and Phenothiazine	3,000,000
of which DDT	49,600,000		
and Hexachlorocyclohexane	8,197,000	*See additional figures in text.*	

Mixed Sprays and Mixed Dusts. It is often desirable to apply two chemicals or even three at the same time, in order to save labor; an insecticide and a fungicide may be mixed, since insects and fungous disease often occur together. Mixed sprays are widely used; thus lime-sulfur, arsenate of lead, and nicotine sulfate may be used together; the same three mate-

[22] The discovery of the fungicidal value of Bordeaux mixture was accidental; while walking in a vineyard, the French scientist Millardet noticed that the vines at the edge of the vineyard had not lost their leaves while the rest had; the custom was to spray the edges with a mixture of copper sulfate and lime in order to scare off thieves who mistook the bluish deposit for poison (1882). This led to experiments by Millardet and Gayon, which established the value of the same mixture as a fungicide.

rials may be used as a dust. Bordeaux mixture, arsenate of lead, and nicotine is another suitable combination. A circular diagram (Fig. 259) indicating the proper choice is given in several government publications and in farm journals. Certain combinations are incompatible, and must be avoided; thus soap solutions must not be used with lime-sulfur.

Disinfectants

The chemical industries perform an important service in furnishing disinfectants which supplement sterilization by steam or flame. The function of a disinfectant is to kill bacteria and to prevent further growth of new cultures. A germicide also kills bacteria, but its power to prevent further growth is secondary; an antiseptic inhibits bacterial growth without necessarily killing.

Among the important chemical disinfectants are: phenol, cresol, guaiacol, thymol, formaldehyde, potassium permanganate, bleaching powder, calcium hypochlorite, sodium hypochlorite, chlorine, bichloride of mercury, aristol, hydrogen peroxide, and mercurial phenols. The standard is a 5 per cent phenol solution; the power of other substances is expressed in terms of the standard, and this value is known as the phenol coefficient. The method is to make a bacterial count before and after application. The phenol number varies with different bacteria.

The Carrel-Dakin solution,[23] discovered during the war of 1914-18, would be classed as an antiseptic; it consists of a 0.5 per cent sodium hypochlorite solution, made from bleaching powder, very slightly alkaline. It is used to irrigate wounds, so that the dead tissue is dissolved, thereby removing the food of bacteria, which die as a consequence.

A 1 to 1000 water solution of hexylresorcinol (*n*-hexyl-2,4-dihydroxybenzene) kills bacteria in 15 seconds; it has a low surface tension, which permits its penetration into small spaces, an important advantage. It is nonpoisonous.

Quaternary ammonium compounds are more and more widely used in restaurants and bars for sanitizing dishes and glassware.[24]

Wood Preservation. The preservation of wood for railroad ties, fence posts, and in general of all wood used outdoors is an important problem. In the past, treating with creosote oil (*see* Chapter 14) has been the chief method, and remains an excellent one. The practice is to heat the wood in order to drive out moisture and air, apply a vacuum to the containing chamber in order to free the pores of the wood, and send in hot creosote, under gradually rising pressure.

In 1947, there were produced in the United States 159,480,000 gallons of creosote oil, a coal distillate, valued at 17 cents a gallon. Essentially all the oil is used for wood treatment. In addition, 65,886,296 gallons of petroleum oils, fortified with preservatives, were consumed in wood preservation.

Other chemical agents used for preserving lumber are zinc chloride, pentachlorophenol, copper naphthenate [25] and magnesium fluosilicate.

[23] "The National Formulary," 8th ed., 1946, p. 483.
[24] "Disinfectants and sanitizers," P. G. Bartlett, *Chem. Ind.*, 64, 215 (1949).
[25] "Developments in wood preservatives," J. Oscar Blew, Jr., *Chem. Ind.*, 64, 218 (1949).

The preserving of wood for marine purposes is a specially vital problem. In certain infected areas, the shipworm causes untold damage in a short time. The *Teredo navalis* and the *Bankia gouldi* are the two best-studied examples of the shipworms. They bore into the wood of piling or ship-bottom and in a short time honeycomb it with burrows so that the wood collapses. The marine piling investigation,[26] conducted by the Chemical Warfare Service has shown in a preliminary way that certain of the war gases, best dissolved in creosote, would be superior agents for marine preservation.

On land, a wooden structure is at the mercy of termites only if the wood touches moist soil to which the termites can retreat. Termites cannot live in dryness, nor in light.

Other Patents

U. S. Patent 2,064,728 and 2,060,311, making colloidal sulfur; 2,044,214, sulfur refining process; 2,046,546-7-8, process for removal of insecticidal residues from fruits and vegetables; 1,928,968, colloidal dispersions of rotenone by the aid of tannic acid; 1,884,542, preparation of arsenical compounds suitable for use as insecticides; 1,875,466, esters of the fatty acids derived from animal or vegetable fats or oils are insecticidal and non-injurious to plant life; 1,877,851, an insecticidal containing petroleum oil, a compound of nicotine with an oil-soluble sulfonic acid derived from petroleum and an emulsifying agent; 1,842,443 and 1,863,519, an insecticide containing aluminum sulfate, potassium hydroxide, and hydrofluoric acid; 1,849,778, a fungicidal distilling composition containing a complex copper salt of mercury thiocyanic acid; 1,890,774, a dust disinfectant, from mercuric chloride, chlorophenol, sodium carbonate and hydrated lime; 1,801,144, disinfectant using 500 parts hydrated lime, 200 parts water, 50 parts mercury acetate; 1,791,430, a fungicide and bactericide consisting of zinc sulfate and lime; U. S. Patent 2,279,879, on mixing powdered carob beans with lead arsenate insecticide to nullify its poisonous effect on humans. U. S. Pat. 2,419,021, bactericidal and algaecidal composition; 2,419,212, wood preserving impregnant.

Reading References

"Comparative efficiencies of components of creosote oil as preservatives for timber," F. H. Rhodes and F. T. Gardner, *Ind. Eng. Chem.*, 22, 167 (1930).

"Insecticidal properties of cryolite and barium fluosilicate," S. Marcovitch and W. W. Stanley, *Ind. Eng. Chem.*, 22, 121 (1930).

"Flotation sulfur in agriculture," Vincent Sauchelli, *Ind. Eng. Chem.*, 25, 363 (1933).

"Ethyl mercury compounds as agricultural disinfectants," W. H. Tisdale, *Ind. Eng. Chem.*, 24, 745 (1932).

"Ethylene oxide and ethylene dichloride, two new fumigants," J. M. Russ, Jr., 22, 844 (1930).

"Analyses of materials sold as insecticides and fungicides during 1930," C. S. Cathcart and R. L. Willis, *N. J. Agr. Expt. Sta. Bull.* No. 513, New Brunswick, N. J.

"Studies on contact insecticides," C. H. Richardson and C. R. Smith, *U S. Dept. Agr., Bull.* No. 1160, May 29 (1923).

"Rotenone," R. C. Roark, *Ind. Eng. Chem.*, 25, 639 (1933).

"Fungicide adjustment, preparation to meet requirements of disease and host," A. C. Sessions, *Ind. Eng. Chem.*, 28, 287 (1936).

"Insecticides and fungicides," R. C. Roark, *Ind. Eng. Chem.*, 27, 530 (1935).

"Phenothiazine as a control for codling moth in the Pacific Northwest gives good results," V. R. Diamond, *Agricultural News Letter* (published by E. I. du Pont Co., Wilmington, Del.), 5, 17 (1937).

"The manufacture, handling and use of hydrocyanic acid," J. P. Carlisle, *Trans. Am. Inst. Chem. Eng.*, 29, 113 (1933).

[26] *Bulletin Am. Railway Eng. Assoc.*, 28, No. 290 (1926).

"Determination of rotenone on derris root and its resin." R. S. Cahn and J. J. Boam, *J. Soc. Chem. Ind.*, 54, 37T (1935).

"Trail solves its sulphur problem," S. D. Kirkpatrick, *Chem. Met. Eng.*, 45, 483 (1938).

"Re-use of bleed water in sulfur mining-reclamation and treatment," D. T. McIver, J. B. Chatelain and B. A. Axelrad, *Ind. Eng. Chem.*, 30, 752 (1938).

A flow sheet on the mining of sulfur appeared in *Chem. Met. Eng.*, 48, 82 (1941).

"Sulfur and national defense," W. W. Duecker, *Chem. Met. Eng.*, 48, 70 (1941).

"Compressed gas aerosols expand their uses," N. C. Cooper, *Chem. Ind.*, 63, 970 (1948).

"Benzene hexachloride," *Chem. Ind.*, 60, 418 (1947).

"DDT," T. F. West and G. A. Campbell, *Industrial Chemist*, 20, 461 (1944).

"DDT fights insects in war and in peace," John R. Callahan, *Chem. Met. Eng.*, 51, 109 (1944).

"Synthetic chemicals for agriculture. Part I: fertilizers and insecticides," R. H. Wellman, *Chem. Ind.*, 62, 914-921 (1948), and Part II: "Fungicides, nematocides, rodenticides and weed killers," *Chem. Ind.*, 63, 223-229 (1948). Each article has a table of common names, chemical names and manufacturers.

"Chemistry and Uses of Insecticides," by E. R. De Ong, Reinhold Pub. Corp., New York, 1948.

A few years ago, the chemist thought of crude rubber as a crop, a gift from nature, harvested under the open sky. Today, the word rubber *brings visions of neat factory yards, assemblies of cylindrical steel tanks, both horizontal and upright, of long lines of gaily painted steel pipes, of ladders, platforms, and brick and steel buildings. Will the new industry born of the desperate war emergency continue, perhaps side by side with harvested rubber, or will this brilliant example of man's resourcefulness be allowed to wilt and disappear? It is the part of wisdom to continue the new industry, so that it may serve us again should the need arise.*

Chapter 39

Rubber

A decade ago, the United States required approximately 600,000 tons of raw rubber for its industries annually. Practically all of this was natural rubber, 98 per cent from the cultivated rubber tree, *Hevea brasiliensis*, and imported mainly from the Far East. During World War II, especially after the fall of Singapore, less and less Hevea was imported, while on the other hand the tonnage of a new material, a manufactured rubber, called into being by war requirements, increased from year to year, until in 1946 there was enough manufacturing capacity (about 1,000,000 tons) for all civilian as well as all military uses.

With the war over, Hevea rubber is coming in again, at favorable prices, and decreasing amounts of synthetic rubber are being manufactured, because Government agencies are withdrawing their support.[1] The sudden drop in the importation of Hevea rubber in 1942, and the equally sudden rise in the production of synthetic rubber during the war years, are shown in Figure 260. Reserves of Hevea rubber permitted a comparatively even rate of consumption. It may be noted here that a certain percentage of natural rubber was compounded with the new synthetic material (GR-S). Reclaimed rubber, both natural and synthetic, contributed a sizable tonnage to the total of available source materials. Sharply increased imports from Brazil, Bolivia, Ecuador, Nicaragua, and Liberia added to the stockpile of Hevea rubber, while Mexico supplied increasing amounts of guayule rubber. Exports of Hevea rubber from Ceylon to the United States continued apparently undisturbed during the war.

There are several types of synthetic rubber. The best known is GR-S, an all-purpose rubber, designed to take the place of Hevea; it made up about 87 per cent of the synthetic rubbers produced during the war years. The specific-purpose rubbers are likely to continue in their normal production

[1] By the Rubber Act of March 31, 1948 (effective until June 30, 1950), the Government retains a high degree of control and continues to operate certain synthetic rubber plants. The Act directs that facilities for producing 600,000 long tons of general-purpose synthetic rubber per year be maintained in stand-by condition, and for 65,000 tons of special-purpose synthetic rubber. The consuming industry is required to absorb 200,000 tons of GR-S and 22,000 tons of special-purpose synthetic rubber annually.

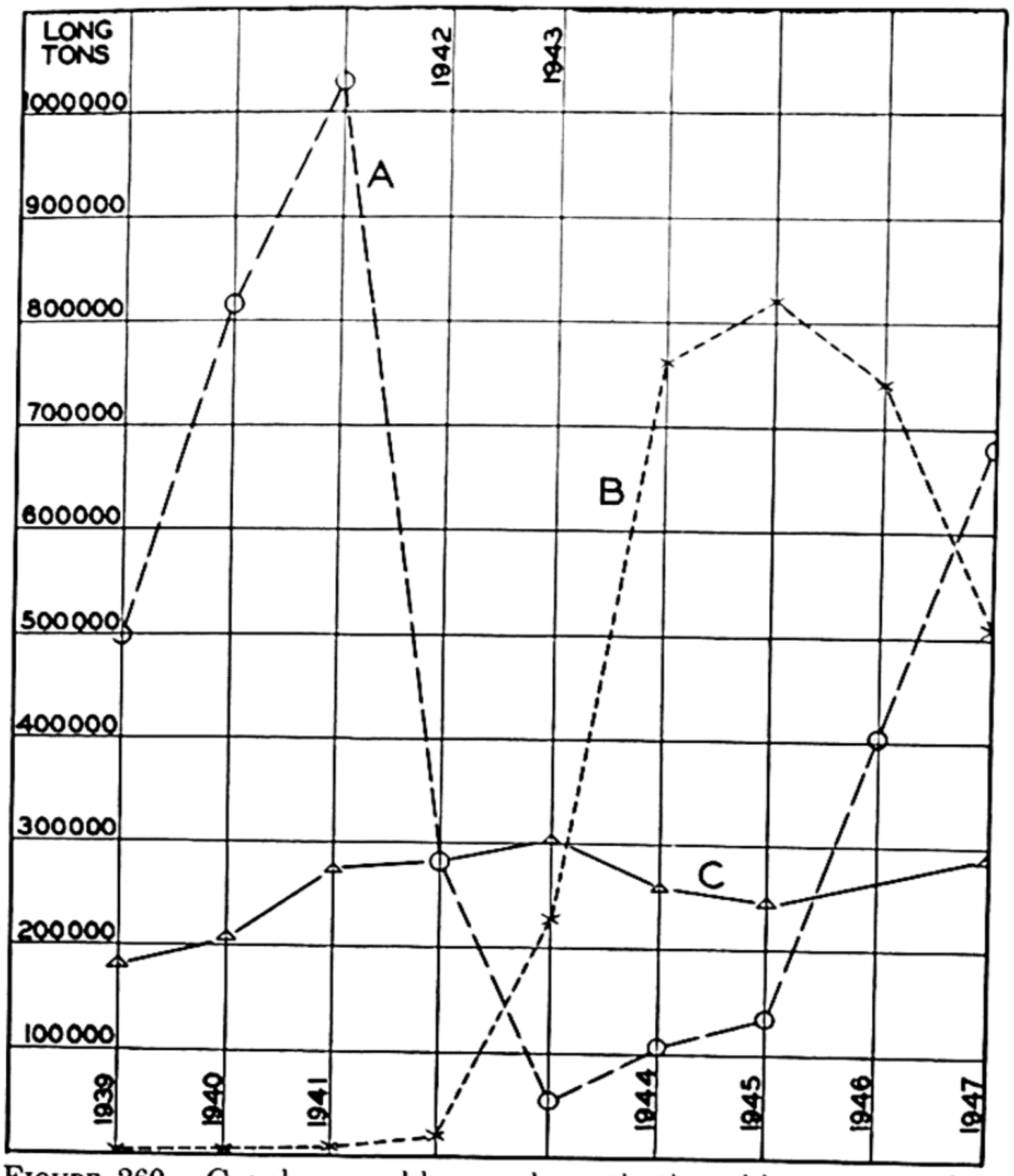


FIGURE 260.—Graph on rubber and synthetic rubber supply figures. A, imports of natural rubber including liquid latex, and guayule, and from all producing areas; B, domestic production of synthetic rubbers, including GR-S, GR-I (butyl) and GR-M (neoprene); C, reclaimed rubber. (Figures partly from Civilian Production Administration, Rubber Division, through "Facts for Industry," 26-1-1, Bureau of Census.)

range, somewhat lower than during the war; they are, among others, neoprene, GR-M; butyl rubber, GR-I; and the butadiene-acrylonitrile rubber GR-A, generally listed with neoprene in Government production statistics. The relative importance in terms of tonnage of these several synthetic rubbers is shown by the plant capacities which the Rubber Reserve Company set up in 1942, raising the earlier figures of May, 1941:

	Desired Capacity
GR-S (all-purpose)	705,000 long tons per year (in 15 plants)
GR-I (butyl)	60,000 long tons per year
GR-M (neoprene)	40,000 long tons per year

These figures were actually realized. The production of GR-S in 1944 was 670,268 tons; in 1945, it was 719,404 tons. For neoprene and acrylonitrile rubber combined, the corresponding figures are 73,472 and 53,543;

while the production of butyl rubber for those years was 18,890 tons and 47,426 tons.

Of the various synthetic rubbers, only neoprene had its process firmly established at the start of the war by over ten years of successful large-scale operation. In contrast, the process for GR-S was based on hurried, concentrated experimentation under the sponsorship of the Rubber Reserve Company. This, together with much of the know-how, sprang from the experience gained by four rubber companies and one oil company in the course of manufacturing special-purpose synthetic rubbers. In the same spirit, the equipment, which the Government made standard for all its 15 GR-S plants, was boldly designed without the customary opportunity to make trials.

After the processes for manufacturing synthetic rubbers, the compounding and curing of Hevea rubber, which is the pattern for the new materials, will be presented.

Manufacture of Synthetic Rubbers

GR-S.[2]* The manufacture of GR-S consists of reacting butadiene (3 lbs.) with styrene (1 lb.) to form straight-chain polymers of controlled lengths. The copolymerization reaction takes place, in the standard installation, in an emulsion of the reactants in a soap solution. The reaction is accelerated by a catalyst, *e.g.*, potassium persulfate ($K_2S_2O_8$). The reactor is jacketed, so that the charge may be heated, at the start, by steam, and later cooled by water or refrigerated water. The reaction is exothermic, and the temperature must be controlled within 0.5° C. (0.9° F.). The lower the temperature, the better the copolymer. A modifier, such as dodecyl mercaptan (DDM), is added to control the quality of the copolymer, which it does by terminating individual chains. The reactor works under pressure and has an agitator. After a number of hours a shortstop is added, such as hydroquinone (HO⟨⬡⟩OH), destroying the catalyst and arresting all further action.

The balance of the operations have for their purpose isolation of the copolymer in the form of a latex; stripping of the unreacted monomers from the latex; creaming of the stripped latex by salt solution and serum; its coagulation by acid; washing with water, filtering, drying, and compressing into bales of 75 pounds. Antioxidants are added after stripping. The recovered monomers are recycled. The copolymerization reaction is:

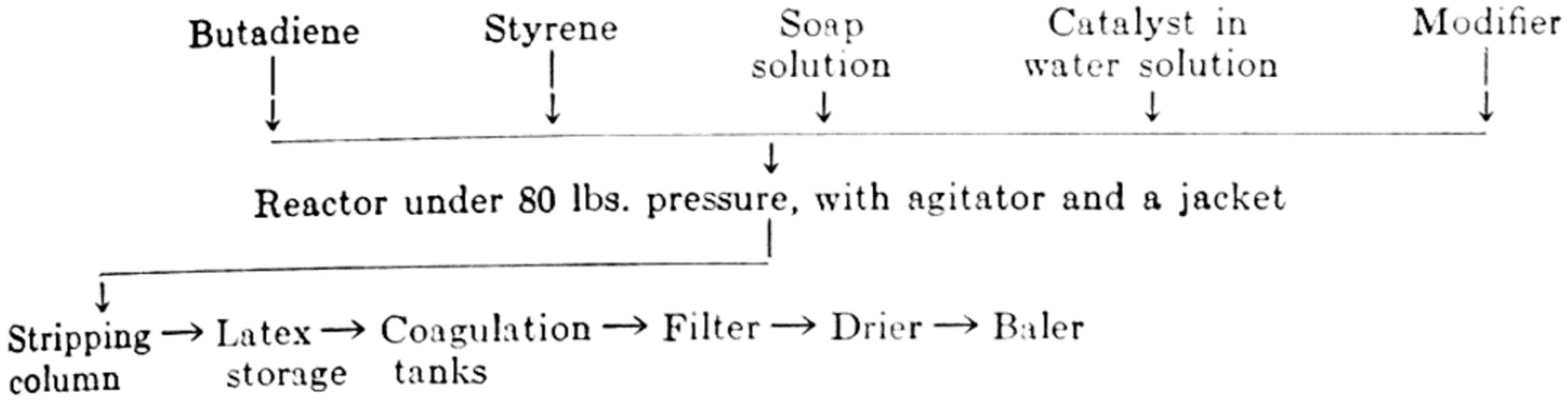
$$n\mathrm{CH_2{=}CH{-}CH{=}CH_2} + n\mathrm{CH(C_6H_5){=}CH_2} \rightarrow [-\mathrm{CH_2{-}CH{=}CH{-}CH_2{-}CH(C_6H_5){-}CH_2{-}}]_n$$

butadiene (a liquid at 60 lbs. pressure) — *styrene* (a liquid) — *Copolymer GR-S* (a soft solid)

[2] Based partly on plant visits, partly on "The preparation and properties of GR-S," by Frank J. Soday, *Trans. Am. Inst. Chem. Eng.*, **42**, 647-664 (1946).

* Reviewed by Frank J. Soday, Research Director, Devoe and Raynolds Co., Louisville 1, Ky.

A highly simplified flow sheet would be as follows:



The heart of the process is the reactor. In a model plant designed for the production of 30,000 long tons of rubber per year, there are two rows of

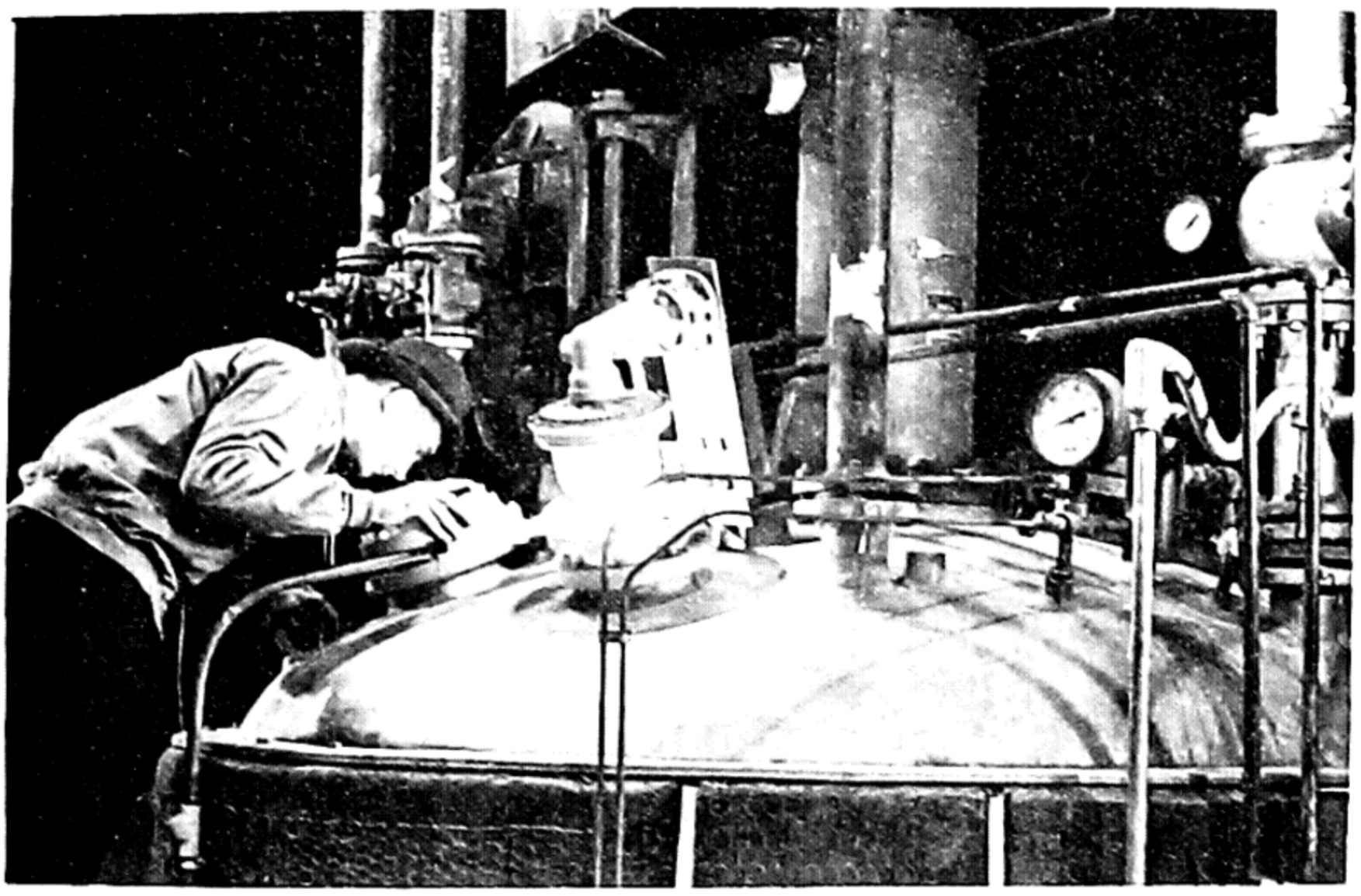


FIGURE 261.—A view of the top of the reactor for manufacturing the synthetic rubber GR-S. Taken at Institute, West Virginia. (Courtesy of the United States Rubber Company, New York.)

12 reactors set in the open. Each reactor is a glass-lined steel pressure vessel of 3785 gallons capacity; it is jacketed, and its agitator has a rotation of 300 rpm. The pressure in the reactor is, for example, 65 lbs./sq. in., and drops to 40 lbs. or so as the reaction proceeds and the amount of butadiene monomer decreases. The temperature is 50° C. (122° F.). The working platform gives access to the top of the reactors, and permits convenient observation of the milky charge through sight glasses, as well as sampling. The metered charge of butadiene, styrene,[3] soap solution (a 6 per cent solution in water of zero hardness) and water are added simultaneously, with the agitator in action, followed soon by the catalyst solution, the modifier, and some flush water.

The hydrocarbons dissolve in each other and form droplets (700 to 1000 Å) suspended in the soap solution, and a portion also dissolves in the

[3] The earlier ratio of 75 to 25 butadiene to styrene is now (July, 1947) 72 to 28. The product contains 22.5 per cent of bound styrene on a hydrocarbon basis.

soap micelles. Copolymerization proceeds; its progress is followed by tests of the viscosity of the emulsion. It is thought that the soap is the actual catalyst, the persulfate functioning like a promoter, which activates it. The initial polymerization takes place in the soap micelle and on the surface of the droplet; after some 20 per cent of the monomers have polymerized, the balance of the reaction takes place within the emulsified droplet. After the

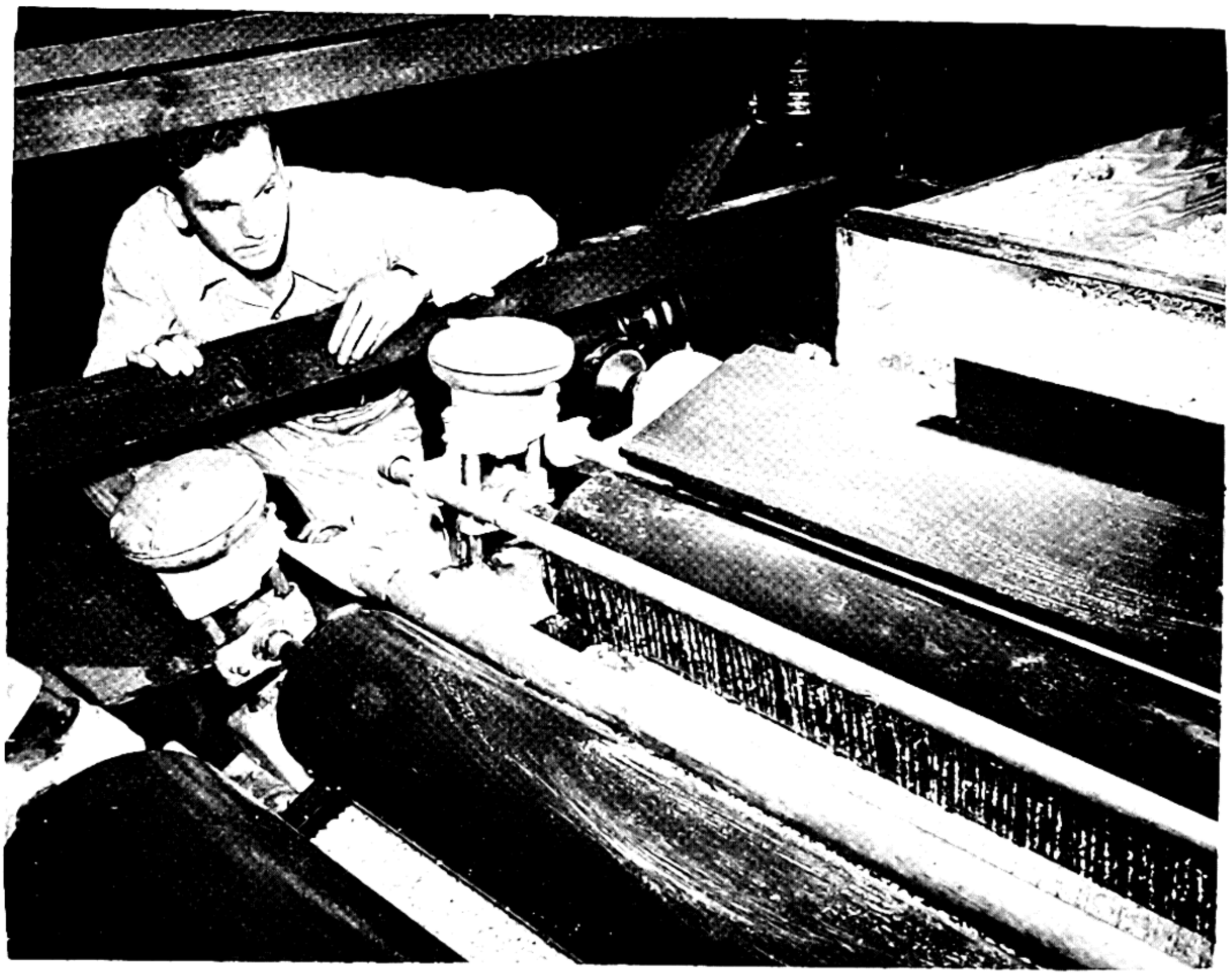


FIGURE 262.—A top view of the Oliver filter on which the crumbs are washed, filtered and pressed relatively dry. The filter is provided with smoothing rolls and press rolls. The water spray between smoothing roll No. 2 and press roll No. 1 is visible. The discharged GR-S blanket goes to a shredder and thence to a warm air three-pass perforated conveyor drier. (Courtesy United States Rubber Company, New York.)

proper period, the shortstop is introduced, and the action comes to an end.

The contents of the reactor are dropped into blow-down tanks (6), each of which has a capacity of 5000 gallons. The blow-down tank is a glass-lined pressure vessel provided with an agitator. The reactor is now ready for the next charge. The cycle is 15 hours. Each reactor produces approximately 6000 pounds of GR-S per charge.

The raw latex passes to a flash tank, where the lower pressure (5 lbs.) permits the release of much of the unreacted butadiene, then to a vacuum flash tank, where the balance is released. All this vapor is compressed and condensed and returned to storage. The latex next passes to the stripping

column fitted with 12 perforated iron trays, porcelain-enameled, and operated under a vacuum. Steam enters at the base and meets the descending latex, stripping it of its unreacted styrene load. Steam and styrene pass out at the top of the column in vapor form, are condensed, separated, and the styrene returned to storage. The conversion in the reactors is 72 per cent, so that about 28 per cent of the reactants must be removed and recovered.

An antioxidant such as phenylbetanaphthylamine (1.5 per cent in the form of a 25 per cent emulsion) is blended with the stripped latex as it issues from the base of the stripping column on its way to large tile-lined concrete storage tanks. From these it is fed to the creaming pump, meeting first a stream of brine which brings about the creaming, thanks to a tenfold increase in the particle size of the copolymer. Upon leaving the pump, the suspension meets a flow of acid which coagulates the particles into crumbs, irregular in size, averaging $\frac{3}{8}$ inch in diameter. The acid has the further effect of liberating fatty acids from the soap molecules on the surface of the copolymer particles while in the holding tank; the stability of the emulsion vanishes, and fairly large, porous aggregates form. These larger crumbs pass over a vibrating screen, losing the accompanying liquor (the serum); the latter serves to dilute the brine and the acid. The crumbs are reslurried in water, filtered and again washed on an Oliver suction filter. The resulting blanket (or cake) is shredded and passed to a Proctor and Schwartz drier (three-pass), where it dries at a temperature not higher than 175° F. (79.5° C.), for a period of two hours. The antioxidant added earlier prevents undue softening of the rubber while in the dryer. The dried product is transferred to automatic scales, and thence to a baler which forms the 75-pound bale. The bale is dusted with soapstone and slipped into a kraft paper bag, in which form it is stored or shipped.

It will be noted that the reactors are operated by batch, while the subsequent operations are continuous. All the steps enumerated may be traced on the complete and elaborate flow sheet (Figure 263). Additional information may be obtained from its study, especially regarding the service of the numerous pumps.

The GR-S in the bale, as it leaves the manufacturing plant, contains 92 per cent pure hydrocarbons, the balance being fatty acids, antioxidants, moisture and approximately 0.5 to 1.0 per cent of inorganic materials, mainly sodium chloride.

Processing, Properties and Structure of GR-S. The properties of GR-S are similar to those of Hevea rubber, but not identical. GR-S is more difficult to plasticize, requiring a longer time on the mill; it responds less to softening agents, and is deficient in surface stickiness. GR-S rubber stocks have relatively low tensile strength and tear resistance and low resilience; also, they exhibit heat brittleness and a certain tendency to crack after repeated bending. These were some of the undesirable properties noted in the early period; as experience in processing GR-S was gained, operators succeeded in varying processing details so that many faults were corrected.

In some respects, GR-S is superior to Hevea rubber: it ages with less change in physical properties; the decomposition temperature of GR-S tread stock is 30 to 60° F. (16.6 to 33.3° C.) higher than that of similar stocks

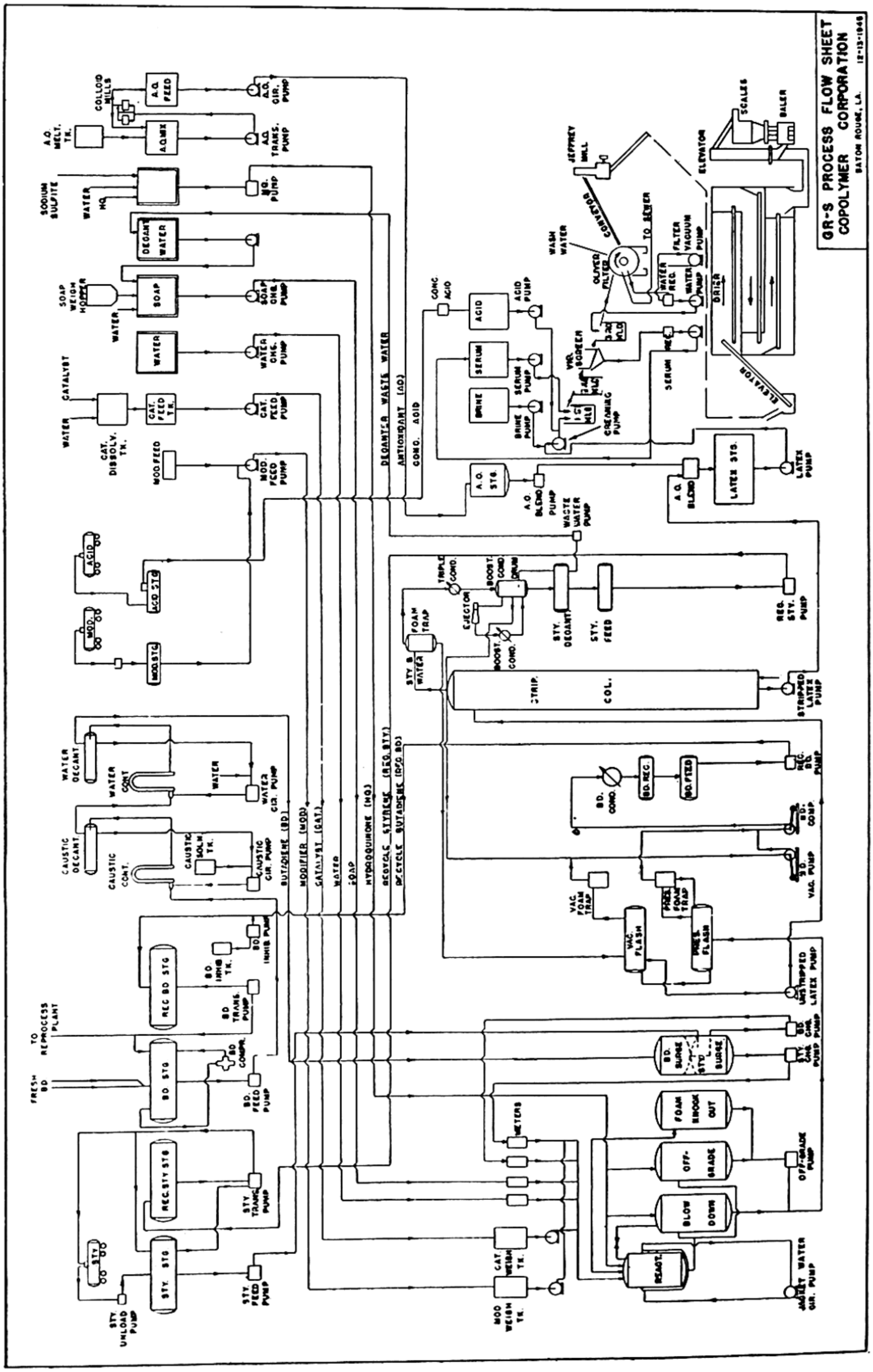


FIGURE 263.—The complete GR-S flow sheet, *Tr. Am. Inst. Chem. Eng.*, 42, p. 653 (1946). (By permission.)

made with natural rubber. In other respects, it is equal to the natural rubber compositions: after it has been plasticized, it tubes and calenders about as well; the temperatures and times of cure are about the same (but the curing tolerance is less); the tire tread wear obtained is at least equal to that of natural rubber treads for passenger-car tires.

For vulcanization, the sulfur ratios vary, in different compositions, between 1.5 and 2.5 per cent of the total synthetic, a lower figure than for similar natural rubber compositions.

Polymer Structure. The following notes on the structure of the polymers will probably prove of interest to the reader: "Natural rubber is a structurally homogeneous polymer of isoprene, while GR-S is a non-homogeneous copolymer of butadiene and styrene. GR-S is composed of butadiene and styrene units in the ratio of approximately 6 to 1, ... but the spacing between adjacent styrene units may vary from 1 to 12 butadiene units. Natural rubber is a *cis*-polymer of isoprene, while GR-S is a mixture of *cis*- and *trans*-copolymers of butadiene and styrene. Gutta percha is a polymer of isoprene having the *trans*- configuration. Natural rubber is a 1,4-polymer of isoprene, while GR-S is a mixture of 1,4- and 1,2-butadiene units."[4] The reaction forming GR-S produces straight-chain polymers up to approximately 20 per cent conversion (see earlier section); some branching occurs at this point and becomes progressively more important; at 78-80 per cent conversion, branching and cross linking are very pronounced.[5]

Several modifications of GR-S have been successfully introduced in the course of the unceasing search for further development and improvement. GR-S 38 stands for GR-S produced by a continuous process; GR-S 50 uses "stalite" as antioxidant, which is non-staining; GR-S 10 is prepared with a rosin soap as emulsifier, and the product, which contains rosin acid, has superior tack; GR-S Black 1 contains carbon black incorporated during the latex stage, before coagulation.

Low-temperature Rubber; "Ultipara." Experimental work carried on in the early forties had shown that the lower the temperature at which the butadiene-styrene copolymerization took place, the better the resulting rubber; also, the lower the temperature, the longer the period for polymerization. Fortunately the latter may be decreased by the use of "speed-up" chemicals. The redox system was developed independently in Great Britain, Germany, and the United States; in this a reducing agent as well as the customary oxidizing agent is added to the batch. In Germany, benzoyl peroxide was the oxidizing agent, sugars the reducing one; rubber of good quality results, but control is difficult. In the United States the method selected for translation into large-scale operation was that of Phillips, producing the polymer at 41° F. The oxidizing agent is cumene hydroperoxide (0.15 parts of charged monomer per hundred by weight); the reducer or activator is dextrose (2.5) with 0.1 ferrous sulfate ($FeSO_4 \cdot 12H_2O$) and 0.6 $Na_4P_2O_7$. The modifier is a tertiary C_{12} mercaptan (0.2). The reaction time was 20 to 22 hours, and the conversion 60 per cent. The product

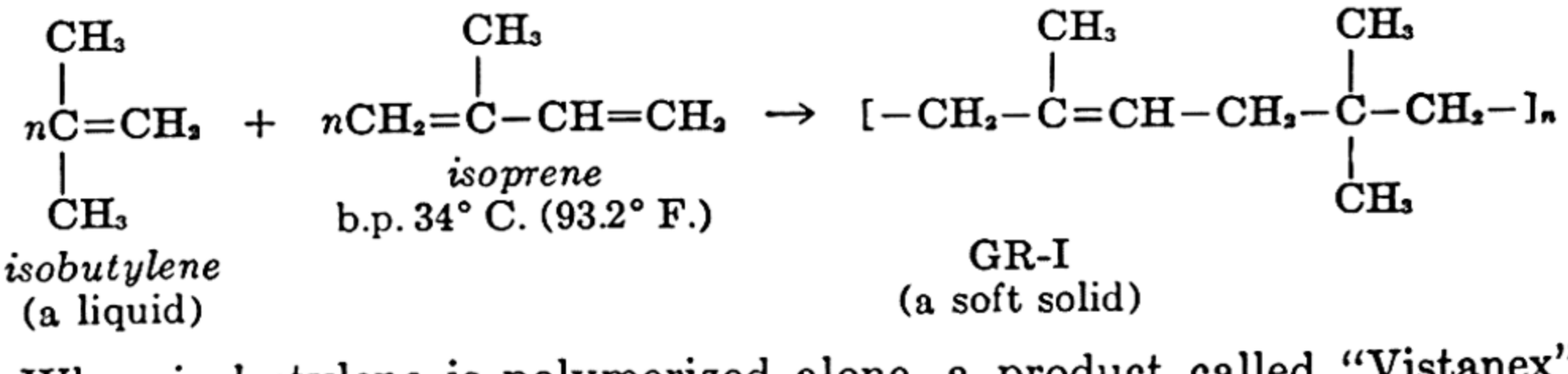
[4] *Tr. Am. Inst. Chem. Eng.*, 42, 659 (1946), article by Frank J. Soday.
[5] Private communication.

is "Ultipara,"[6] a synthetic rubber which yields vulcanizates superior to those from GR-S in tensile strength, elongation, flex life, resilience, resistance to artificial aging and to crack-growth tendencies. The latter is one of the characteristics of GR-S. The 41° F. polymer is being made at the rate of more than 15,000 tons per year (May, 1949). Work is going on in the study of the 14°, 0°, and −4° F. polymers. Means to lower the reaction time for "Ultipara" are being sought vigorously.[7] Another designation for "Ultipara" is "X-478" rubber. It is planned (June, 1949) to convert a sufficient number of Government-operated plants to produce 200,000 tons of cold rubber by early 1950.

Just as Hevea latex was widely used as such before the war, so were synthetic rubbers latices during the war. For example, GR-S Type III is an all-purpose latex made from equal parts of butadiene and styrene; it is well suited for making sponge rubber and cellular rubber.

GR-I or Butyl Rubber. Butyl rubber, or GR-I, is a copolymer of isobutylene and isoprene, with the latter in low proportion. It is remarkable for several reasons, one of which is the low temperature at which it is produced. Into the reactor are fed pre-cooled isobutylene, isoprene, and a solvent or diluent in which the catalyst is dissolved; the temperature is held to between −95 and −103° C. The materials are well mixed by an agitator. Reaction takes place immediately, with generation of heat which is removed by the refrigerant (liquid ethylene). A special lubricant on the agitator and special packing, which remains soft at the low temperature, are employed. The catalyst is a compound of the Friedel-Crafts type. The product leaves the reactor in the form of minute crumbs which are freed of solvent and washed in water.

Butyl rubber resembles natural rubber in appearance; it is unsaturated, and therefore can be vulcanized. Hard rubber cannot be made from it, however, as the unsaturation is too low (3 per cent). Butyl rubber cannot be made in the form of latex. It is compounded and handled very much like GR-S. As butyl is the least permeable to gases of all rubbers, most of it is consumed in automobile inner tubes. It is prized also for making the air bags for curing tires. The reaction for its synthesis is:



When isobutylene is polymerized alone, a product called "Vistanex" is formed. This may vary from a soft, sticky gum to tough, elastic materials, depending upon the degree of polymerization. "Vistanex" cannot be vulcanized. It is used mixed with other rubbers for tire treads, electrical insulation for high-voltage wires, for making adhesives, and many other pur-

[6] Made by the Copolymer Corporation, in a Government-owned mutual plant.
[7] "Low-temperature manufacture of chemical rubber," Will H. Shearon, J. P. McKenzie and Martin E. Samuels, *Ind. Eng. Chem.*, 40, 769-777 (1948).

poses. The seal strength of wax wrappings for frozen foods is improved by blending "Vistanex" with the coating wax.

GR-A. GR-A is a butadiene acrylonitrile copolymer, produced very similarly to GR-S. Butadiene and acrylonitrile are combined in somewhat varying ratios to form the synthetic rubbers known as "Hycar" OR-15 and OR-25, "Chemigum" N, "Butaprene" N, "Paracril," "Perbunan," and others. Acrylonitrile is made from ethylene oxide and hydrocyanic acid (HCN). "Chemigum" N 3, for example, is made by reacting 55 parts of butadiene and 45 parts of acrylonitrile, and adding 2 per cent of phenylbetanaphthylamine. The specific gravity is 1. GR-A has residual unsaturation, and thus may be vulcanized.

$$n\mathrm{CH_2{=}CH(CN)} + n\mathrm{CH_2{=}CH{-}CH{=}CH_2} \rightarrow [-\mathrm{CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH(CN)}-]_n$$

Acrylonitrile — *1,4-Butadiene* — (a soft solid) GR-A

The GR-A rubbers resist the action of petroleum oils, gasoline, vegetable and animal oils and fats, and solvents. Mixed with other rubbers, or with reclaim, they give a variety of valuable properties, such as resistance to low and high temperatures [−70 to 300° F. (−57 to 149° C.)].

Nearly all rubbers which are vulcanizable will yield hard rubbers by incorporating sufficient sulfur. "Hycar" OR-15 and OR-25 may be made into sponge rubber also. These two processes may be combined, to give a cellular hard rubber, weighing only 6 to 8 lbs. per cubic foot, which will sustain a load of several hundred pounds per square inch.

GR-M or Neoprene. Neoprene is polymerized chloroprene. The raw materials for making the monomer are acetylene and hydrogen chloride.

In a preliminary operation, vinylacetylene is prepared as follows: Acetylene, preferably piped from a nearby carbide plant and purified by washing in concentrated sulfuric acid, is swept through a concentrated solution of cuprous chloride with ammonium chloride, held at room temperature. The issuing gas is cooled to −70° C. (−94° F.), when the vinylacetylene ($CH{\equiv}C{\cdot}CH{:}CH_2$) with boiling point of 5° C. (41° F.), is condensed, while the excess acetylene is allowed to pass on for re-use. The condensate is distilled in a column; the overhead gives pure vinylacetylene, while the bottoms contain divinylacetylene. The purpose of the rapid sweep through the catalyzing solution is to avoid the formation of undue amounts of divinylacetylene.

Chloroprene is made by passing vinylacetylene in gaseous form through a solution of cuprous chloride (25 parts) and ammonium chloride (25 parts) in concentrated hydrochloric acid, contained in reactors—horizontal cylindrical vessels. For the sake of safety, the reactors are erected in stalls having concrete side walls, but no end wall and no roof. The reactors are maintained at 30° C. (86° F.). The product [chloroprene, 2-chloro-1,3-butadiene, $CH_2{:}CCl{\cdot}CH{:}CH_2$, boiling at 59.4° C. (139° F.) at atmospheric pressure] is swept out at once by a stream of hydrogen chloride, to prevent the addition of a second molecule of hydrogen chloride. The gases issuing from the reactor are cooled, the chloroprene condensed, mixed with a small amount of

pyrogallol and distilled with steam at reduced pressure (100 mm). The yield based on acetylene is about 65 per cent. The uncondensed hydrogen chloride is utilized again.

There are sixteen different neoprenes and neoprene latices on the market at this time, so that one set of specific data applying to all could not be given. The polymerization, therefore, will be described in general terms.

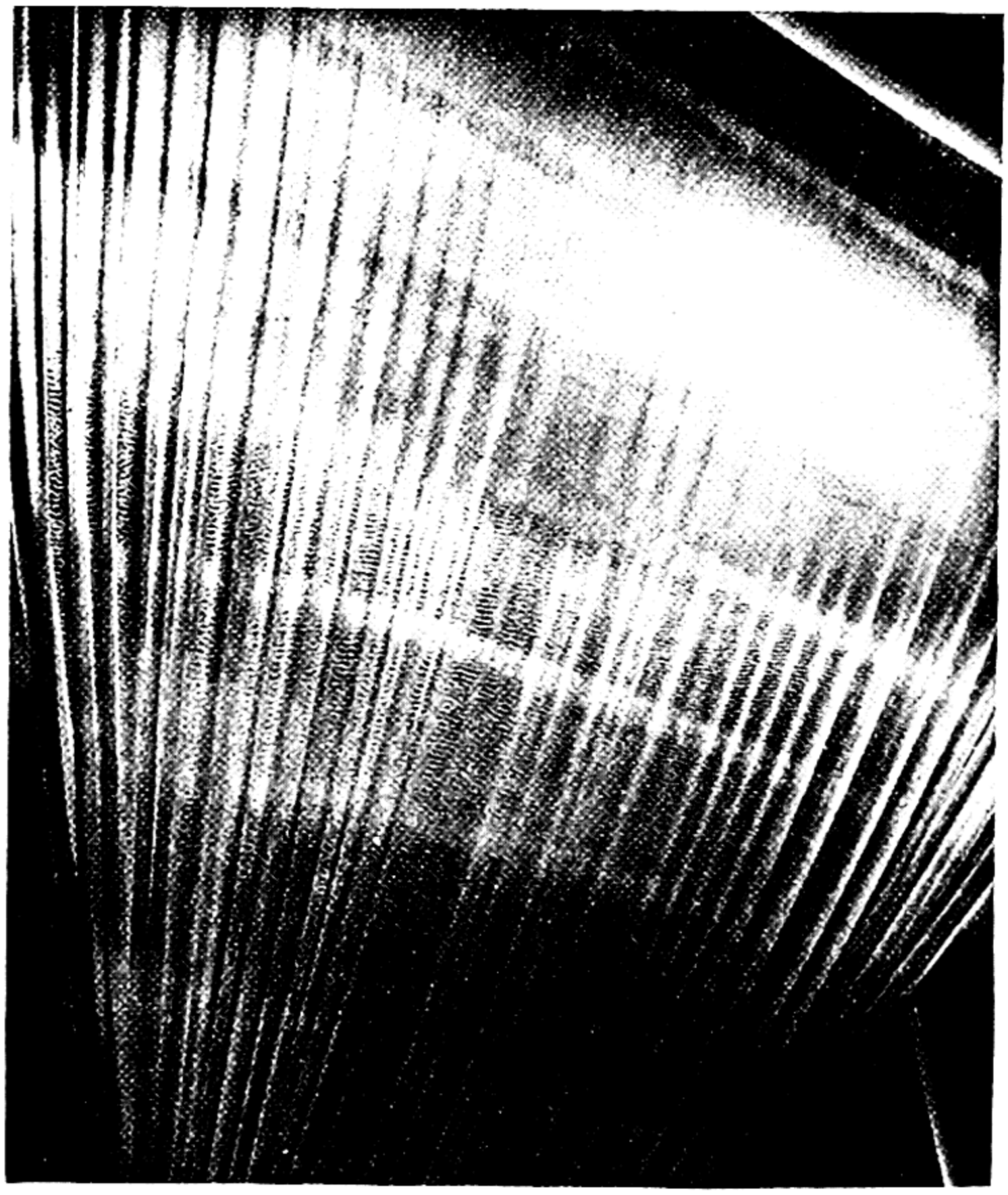


FIGURE 264.—The air-dried film of neoprene formed by coagulation of the latex on the freeze roll, and dried, as it leaves the dryer, on its way to the roping device. (Courtesy of E. I. du Pont de Nemours and Co., Rubber Chemical Division, Wilmington, Del.)

For the preparation of the polymer, the method now in general use (1947) involves coagulation by freezing.[8] The first step is the emulsification of the liquid monomer in a water solution of sodium abietate. The emulsion is heated to a medium temperature for less than 2 hours, to bring about polymerization—a spontaneous process which transforms the droplets of chloroprene into particles of soft rubber. By varying the time and other factors, the degree of conversion may be controlled. In coagulating the

[8] "Continuous isolation of GR-M from latex," M. A. Youker, *Chem. Eng. Progress*, 43, 391 (1947).

particles, no coagulant to form crumbs, is added, as for GR-S and other rubbers. Instead, the latex, with 35 per cent polymer content, is fed to a freeze roll pan for "slow" freezing at −12 to −10° C. (10.4 to 14° F.), after adjusting the pH to 6. A continuous sheet of polymer film and ice crystals 6 feet wide is sheared off the freeze roll, thawed, washed with filtered water at 30° C. (86 °F.), squeezed between rolls, and dried in a Proctor and Schwartz multipass air-lay drier. The dried film is guided by two fingers to a female and a male roll and there compressed into rope form, about 1½ to 2 inches thick, cut into 14-inch lengths, and dropped into bags holding 50 pounds.

The plasticity of the product is controlled by the rate of freeze and the thickness of the film; the softer polymer requires a slower speed and greater thickness. The reactions are:

$$2CH\equiv CH \rightarrow HC\equiv C\cdot CH:CH_2;$$

acetylene (a gas) — *vinylacetylene* (a gas above 5° C.)

$$CH_2:CH\cdot C\equiv CH+HCl \rightarrow ClCH_2\cdot CH:C:CH_2 \rightarrow CH_2:CCl\cdot CH:CH_2$$

chloroprene

$$n CH_2:CCl\cdot CH:CH_2 \rightarrow (-CH_2\cdot CCl:CH\cdot CH_2-)_n$$

monomer (a liquid) — *polychloroprene* (polymer, a soft solid)

The first or α-polymer is plastic. On storing for a limited time, such as two or three months, it hardens, but may be rendered plastic again by mastication. The plastic polymer is transformed into the μ-polymer, the cured or vulcanized rubber, by heating it in the presence of zinc oxide, or such other substances as zinc chloride, magnesia, aniline, naphthylamine, or benzidine. Heating the α-polymer alone to 130° F. (54° C.) for a few minutes changes it to cured or vulcanized rubber.

The plasticity of the first polymer may be preserved indefinitely by mixing with it some diphenylguanidine.[9] The chloroprene latex may be preserved as such by adding sulfonated abietene.

The great value of neoprene is its resistance to gasoline, to liquid propane and butane, and to petroleum oils. Neoprene is also used to advantage in making wire insulation, cable jackets, high-quality garden hose, gaskets for aliphatic liquids, for belts for power transmission and for conveyor belt covers where oil and heat are encountered.

"Thiokol." This product, named from the Greek word for sulfur, *thion*, is the class name of a group of substances, all rubber-like, produced by the action of an organic dihalide with sodium tetrasulfide:

$$n CH_2Cl-CH_2Cl + n Na-S-S-Na \rightarrow (-CH_2-CH_2-S-S-)_n + 2n NaCl$$

ethylene dichloride — *sodium tetrasulfide* — *"Thiokol" A*

The reaction is generally carried out by running the organic dihalide into an aqueous solution of the inorganic polysulfide. The organic polysulfide polymer separates out, forming a latex, which may be coagulated or worked

[9] U. S. Pat. 2,002,622.

up in other ways. The coagulum is washed free of sodium chloride. The raw "Thiokol" is compounded, processed and vulcanized to form rubber-like products, or it may be made into molding powder and hot spray powder. The vulcanizing agent is zinc oxide, in amounts, for example, not exceeding 10 per cent. "Thiokol" is the most oil-resistant of all synthetic rubbers. Type FA compounds are practically unaffected by motor gasoline, fuel oil, kerosine, lubricating oils and other petroleum hydrocarbons, and by a number of alcohols, ketones and esters. "Thiokol," like neoprene, is an American development, and these were the first synthetic rubbers produced commercially in the United States.

TABLE 143.—*Commercial introduction of synthetic rubbers.**

Type	Country	Year
Methyl rubber, from 2,3-dimethyl-1,3-butadiene	Germany	1915
"Thiokol"	U. S. A.	1930
Neoprene (originally called "Duprene"	U. S. A.	1932
Butadiene rubber, with butadiene made from alcohol	Russia	1932
A X F	U. S. A.	1934
"Koroseal"	U. S. A.	1935
Buna 85 and Buna 115, sodium polymers (small scale)	Germany	1935
Buna S and Perbunan (Buna N), emulsion polymers	Germany	1937
"Vistanex"	Germany	1938
"Ameripol," "Hycar," "Chemigum" and Butyl	U. S. A.	1940
"Norepol," "Agripol," GR-S	U. S. A.	1942

* "Modern Plastics Encyclopedia," Vol. 1, p. 232, 1947.

The chief use of "Thiokol" is in gasoline hose linings, in paint spray and lacquer hose, and in sheeting. Hot spray powders are used for coating a metal or similar surface by spraying through a hot flame, such as in the Schori hot flame process.

Latex Foam, or cellular rubber, is made from latex, to which there has been added a frothing agent (such as castor oil soap) and into which air has subsequently been beaten.[10] The additions are ethyl zymate, soap, zinc oxide, clay, sodium silicofluoride and carbon black to produce the grey color. The coagulant, sodium silicofluoride, is added last, and the whole poured into forms or molds, which move on a conveyor to the curing chambers. The conveying time is 22 minutes, during which time the rubber forms a tight gel. The molds travel through the curing chamber, heated by steam, for a period of 45 minutes, after which the cured and finished "Pillo-Foam" pieces are removed, washed, centrifuged and dried with warm air. The volume of air in this cellular rubber is 4 to 5 times that of the rubber.

RECLAIMED RUBBER

Rubber from discarded, worn-out tires made from either natural or synthetic rubber, may be reclaimed to yield a product which is one of the most useful raw materials in the rubber industry. The tires are mechanically cracked and finely ground, ferrous metal being removed magnetically; then the scrap is digested in a pressure vessel, in water containing defibering and reclaiming agents. The defibering agents may be dilute metallic chlorides

[10] U. S. Pat. 1,777,945, 1,828,481, 1,852,447 and 1,994,503.

or caustic soda, and the reclaiming agents are usually petroleum and coal tar-base oils and resins. The digestion may continue for 5-24 hours at 370-405° F. It decomposes the fabric and devulcanizes or partially depolymerizes the rubber, which is then washed, dewatered, dried, blended, strained to remove nonmagnetic metal, and refined.

A refiner is similar to a two-roll mixing mill, but is operated with a high surface speed ratio with the rolls very close together. The paper-thin sheet of reclaimed rubber is wound up on a drum and the accumulated layers cut off in slab form. It is then ready for shipment to the manufacturer of rubber goods, who compounds and vulcanizes it just as he does new rubber. It may be used either with or without new rubber, depending on the nature and cost of the article. In 1947 the consumption of reclaimed rubber in the United States was 289,000 long tons, or 28.5 per cent of the consumption of natural rubber and GR-S (Buna-S) combined.

Hevea Rubber

In order to indicate the true relative importance of the several natural rubber-producing areas of the world, it is necessary to go back to 1940, when conditions were still normal, and there had been no dislocation due to the war. In that year, the rubber-producing areas of the world were as follows: British Malaya, 540,417 long tons; Netherlands East Indies, 536,740; Ceylon, 88,894; Indo-China, 64,437; Thailand, 43,940; Sarawak, 35,166; India and Burma, 23,317; North Borneo, 17,623; South America, 17,601; Africa (except Liberia), 10,103; Liberia, 7223; Mexico (guayule) 4106; Oceania, 2267.

The stimulation brought about by the war demand for rubber led to greatly increased production in unoccupied areas, as shown by the figures in Table 144.

Table 144.—*Imports of natural rubber and latex into the United States.**
(Long tons, dry weight basis)

	1939	1940	1945
Latin America and West Indies	7,986	11,061	37,620
Bolivia	242	216	3,257
Brazil	4,696	5,592	17,170
Mexico (guayule)	2,233	3,634	10,009
Africa	5,517	7,314	35,703
Belgian Congo	—	243	3,653
French Cameroons	—	—	2,821
French Equatorial Africa	—	—	3,326
Liberia	5,331	6,917	20,311
Ceylon	34,818	55,001	64,245

* Bureau of the Census, Washington, D. C.

The *Hevea brasiliensis* tree, the source of practically all natural rubber, is cultivated in plantations in Malaya, and these plantations are the models for all others.[11] The tree resembles the maple in size. Trees are tapped

[11] An historical note on the early plantings of Hevea seedlings, and on the history of vulcanization, will be found in the fourth edition of "Industrial Chemistry," in the chapter prepared in close collaboration with Mr. Raymond B. Stringfield, Consulting Chemical Engineer, Los Angeles, Cal.

after they are six years old, and until over forty. Native tappers remove a shaving of bark from a diagonal cut extending one-third around the tree, and collect in small cups the latex which flows out. The trees are tapped every other day, yielding about an ounce of latex. The latex, which averages about 35 per cent rubber in the form of particles 1 to 2 μ in diameter dispersed in a watery serum, is brought to a collecting station, diluted to about 15 per cent rubber content, and coagulated by addition of acetic or formic acid.[12]

The bulk of the rubber comes on the market as ribbed smoked sheet. This is made by sheeting the coagulated rubber on even-speed rolls with light washing, and drying from 7 to 11 days at 40 to 50° C. (104-122° F.) in an atmosphere of smoke from burning fresh wood. The smoke turns the rubber brown, and acts as a preservative, preventing the development of mold in the serum substances remaining in the rubber. The smoked sheets are pressed into square bales of 200 to 220 pounds, and protected with plywood for shipment.[13]

Another important grade of rubber is pale crepe. For this, sodium bisulfite is added to the latex before coagulation, and the coagulum washed thoroughly on differential-speed rolls to tear the rubber apart and remove serum substances. The sheets are then dried without smoking, yielding a yellowish-white rubber which is baled as before. Other lower grades, such as brown crepe, blanket crepe, rolled brown, and plain unsmoked sheets are made by various plantations.

Variations in supply and demand, coupled with arbitrary economic restrictions, have caused the price of rubber to fluctuate between a high of \$1.25 per pound in 1925 and a low of $2\frac{5}{8}$ cents per pound in 1932. Plantation operations have been greatly improved, and where in 1920 plantation costs were approximately \$0.21 per pound, it is now estimated that, except for war's interference, rubber could have been landed in New York from the better plantations to sell profitably at 7¢ per pound. The high and low for 1947 were approximately $25\frac{3}{4}$¢ and 14¢, respectively. Over the war years, GR-S was held at $18\frac{1}{2}$¢ by the Rubber Reserve Board; at this time (January, 1948) it sells just under that figure.

Vulcanization. Raw Hevea rubber mixed with 3 per cent more or less of ground sulfur, and heated, undergoes a change called vulcanization. Contrasted to raw rubber, vulcanized rubber is no longer tacky, is much stronger, resists abrasion, and is swelled but not dissolved by solvents. Vulcanization is a progressive reaction; it should be allowed to continue to a definite point, and not beyond. The time for vulcanization (120 minutes at 287° F. [141.7° C.]) for rubber and sulfur alone, may be shortened by adding certain organic substances, singly or in combinations, in amounts varying from 0.1 to 1.5 per cent. The time of curing has been reduced, to give an extreme example, to as little as 3 minutes at 200° F. (93.3° C.). Commonly used

[12] The rubber latex particles exhibit a lively Brownian movement visible in the ultramicroscope. The particles are spherical in the latex from young trees, slightly egg-shaped if from older trees. One view is that the particle carries a drop of hydrocarbon oil contained in a sack made of the same oil but gelatinized, and the whole stabilized on its surface by a protein layer.

[13] The name of the plantation is embossed in the sheet.

accelerators are mercaptobenzothiazole ("Captax") $C_6H_4 \cdot N:C(S)SH$; diphenylguanidine (DPG) $(C_6H_5NH)_2C:NH$; tetramethylthiuramdisulfide ("Tuads") $(CH_3)NCS \cdot S \cdot S \cdot CSN(CH_3)_2$, and zinc dimethyldithiocarbamate ("Zimate") $[(CH_3)_2NCS \cdot S]_2Zn$.

Deterioration of vulcanized rubber is retarded by adding other organic substances in amounts of 1 per cent or so. Examples of such antioxidants are aldolalphanaphthylamine and phenylbetanaphthylamine.

Compounding: The art of mixing other ingredients with rubber and of processing the mixed compound is called "compounding." [14] Other ingredients, in addition to sulfur, accelerators and antioxidants, are accelerator activators (for example, 1 to 5 per cent of zinc oxide plus 1 per cent of stearic acid), accelerator retarders (salicylic acid), rubber substitutes, softeners, odorants, colors, fillers, and pigments.

Mixing of the compounding materials is sometimes done on open mill rolls, but more often in the internal mixer called the "Banbury," the various materials being added one by one in the selected order. Raw natural rubber is tough, and requires mastication until it is hot and plastic before compounding ingredients can be added, and the compound sheeted or shaped for the next operation; the same is true of GR-S. Softeners such as vegetable or mineral oils, waxes, tars, pitches and resins are added to save time and power and to facilitate handling.

As "pure gum" products, that is, pure vulcanized rubber products, are too soft and elastic for most commercial uses, reinforcing agents are commonly added to the rubber; they increase the hardness, stiffness, tensile strength, and resistance to cutting, tearing and abrasion. Their action is purely physical, and is due chiefly to their fine particle size and good dispersion in the rubber. The most important reinforcing agent is carbon black made by the channel process; it is used in all articles which receive extremely rough service, such as tire treads and conveyor belts. Furnace blacks ranging in particle size from coarse to the fine furnace grades are also extensively used, the former for tire carcass and mechanical goods, and the latter for tire treads, to impart abrasion resistance comparable to channel black. Zinc oxide is used when the stock must be light-colored; it is not as effective as carbon black, and is much more expensive on a volume basis. Many nonreinforcing fillers, such as whiting, clay, or slate flour, may be used in certain places to add weight, stiffness, reduce elongation, improve processing or reduce costs. Such uses are entirely legitimate; there is no object, for instance, in having high abrasion resistance in a product not subjected to rough usage. Pigments, dyes or lakes are used where colored products are desired.

The compounding formula for four typical stocks, natural rubber tread, Buna S tread, natural rubber tube and butyl tube, are given in Figure 265,

[14] For comparison purposes, it is customary to calculate all formulas for rubber compounds in per cent by weight on the weight of the rubber present, or in volumes of filler per 100 volumes of rubber. The latter is particularly useful as it takes into account the specific gravity of the materials used. Thus rubber has a sp. gr. of 0.92, ZnO 5.57, and carbon black 1.80, and either 55.7 lbs. of ZnO or 18.0 lbs. of carbon black would be a 10 volume loading when mixed with 92 lbs. of rubber.

with a set of stress-strain curves for these same stocks after vulcanizing at the temperature and for the period (in minutes) specified on the graph.

Stock Preparation. The main operations in preparing rubber stock are milling, calendering and extruding or "tubing." The rubber compound is milled for two purposes: to mix and thoroughly disperse the ingredients, and to plasticize the rubber and render it more adaptable to later operations.

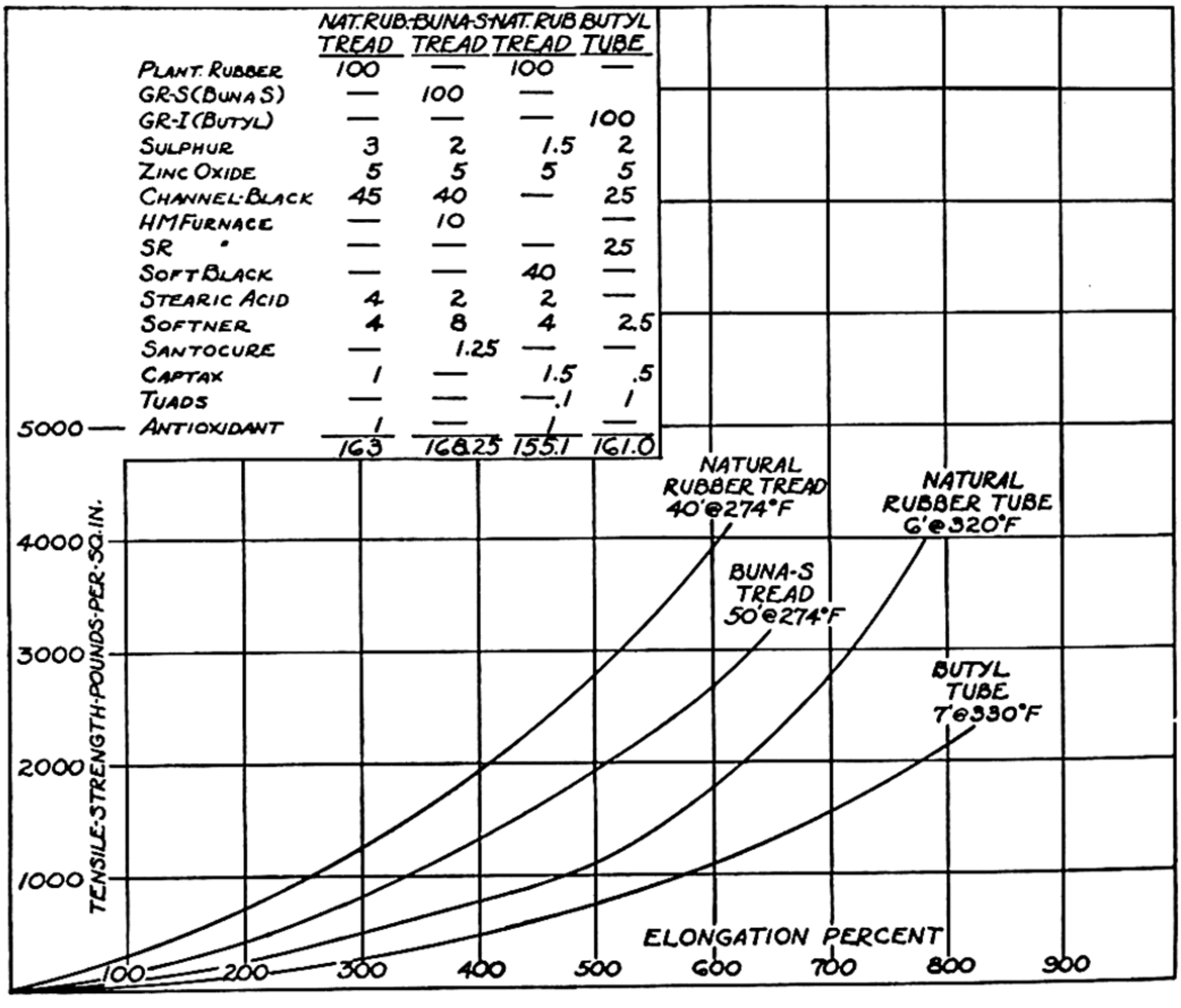


FIGURE 265.—A set of stress-strain curves of typical modern rubber stocks; above are the four formulas for the compounding, all based on 100 parts of gum rubber. Note: In the third column, read "Tube" instead of "Tread." (Courtesy of the Dunlop Tire and Rubber Co., Buffalo, N. Y.)

The milling is done on internally cooled mixing rolls, 84 inches long and 22 or 26 inches in diameter, of cast steel, with hand manipulation; or in a Banbury mixer, which is enclosed and completely mechanical. The mixing rolls consist of two differential rolls mounted together horizontally, geared to revolve at a ratio of about 1 to 1.25, the surface speed of the slow roll being 95 feet per minute. Rubber placed on the rolls is squeezed downward through the "bite," and allowed to sheet around the slow roll and back into the excess or "bank" on top of the rolls. One roll is adjustable to vary the thickness of the sheet between $\frac{1}{8}$ and $\frac{3}{8}$ inch.

When the rubber is soft enough, the other ingredients are added, in

proper order, the operator working the batch from time to time by cutting the sheet on the roll to bring fresh material through the bite. A batch may vary from 50 to 350 pounds, depending on its type, and making may require from 10 to 60 minutes. Much heat is developed; when mixing is completed, the sheet is cut in slabs 3 feet square and dipped in a slurry of talc and water or soap solution to cool and prevent sticking together. Similar mills are used for sheeting out stock issuing from Banbury mixers.

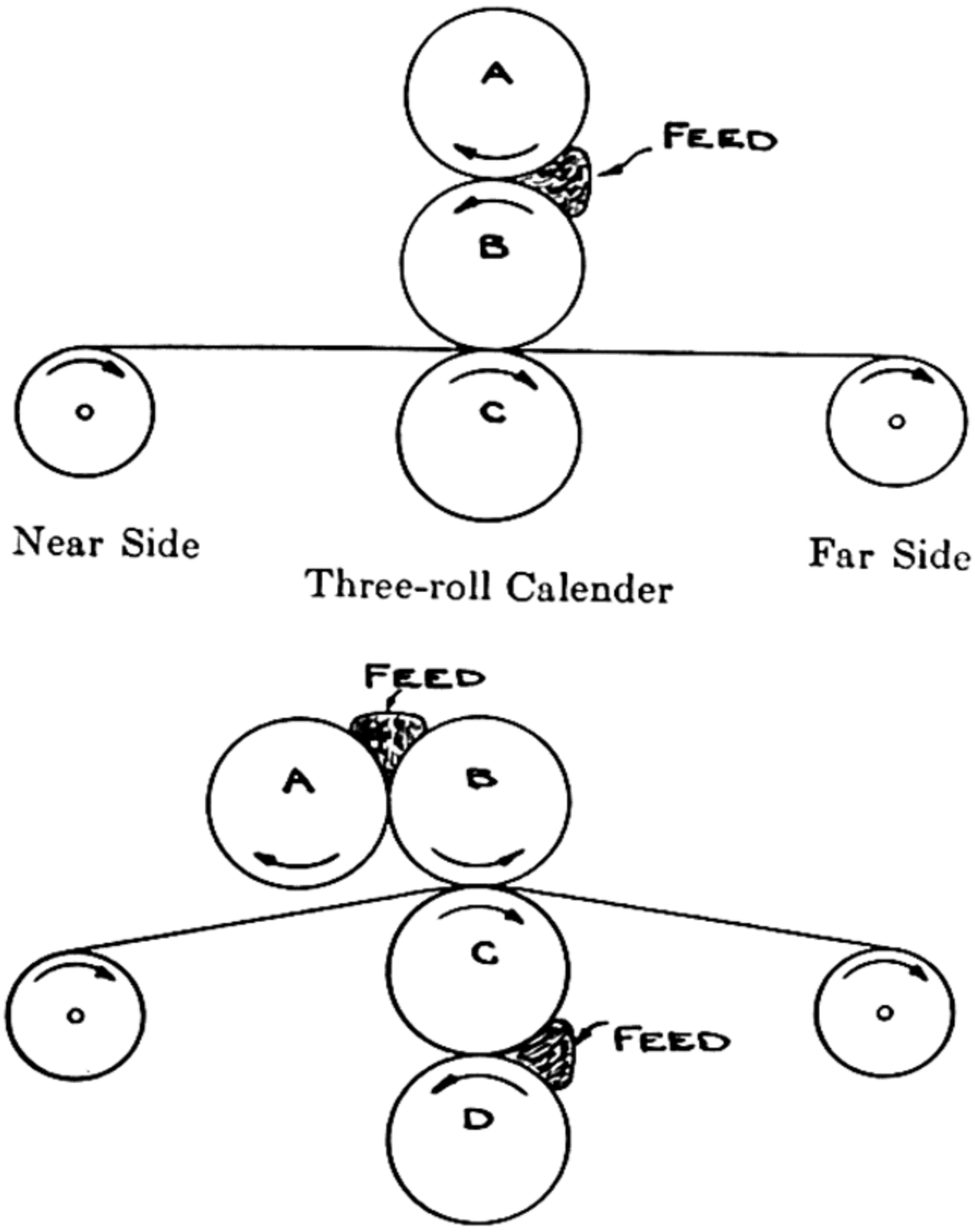


FIGURE 266.—Diagrams of a three- and four-roll calender (see text).

The Banbury mixer is an enclosed machine with two water-cooled mixing rotors operating in a water-cooled chamber. There are various sizes of Banbury mixers.[15] Mixing is rapid; for example, an 84-inch mill will mix a 300-pound batch of tread stock in 30 minutes, while a number 11 Banbury will handle 400 pounds of the same stock in 8 minutes. Mixing in a Banbury saves not only time and labor, but also power. It should be observed furthermore that the many pounds of carbon black for tire tread stock may be added rapidly by means of a screw conveyor into the closed mixer, with a minimum generation of dust.

Calenders may be three or four roll machines (Fig. 266) and are used for three general types of work: *frictioning*, *skim-coating* and *sheeting*. Cot-

[15] For illustrations of the Banbury mixer, of the heavy-duty mixing rolls, with fuller descriptions, see Chapter 11 in "Chemical Machinery," by Emil R. Riegel, Reinhold Publishing Corporation, New York, 1944.

ton fabric is "frictioned" by passing it over roll C with roll B running at a higher speed, resulting in wiping the rubber compound into the voids in the fabric. "Skimcoating" is a similar operation, but with roll B at the same speed as C so that a film of rubber is pressed into the fabric. For "sheeting," roll C is lowered and a cotton liner used, the sheet of rubber formed between A and B being led into the liner, in which it is wrapped. Rayon fabric is

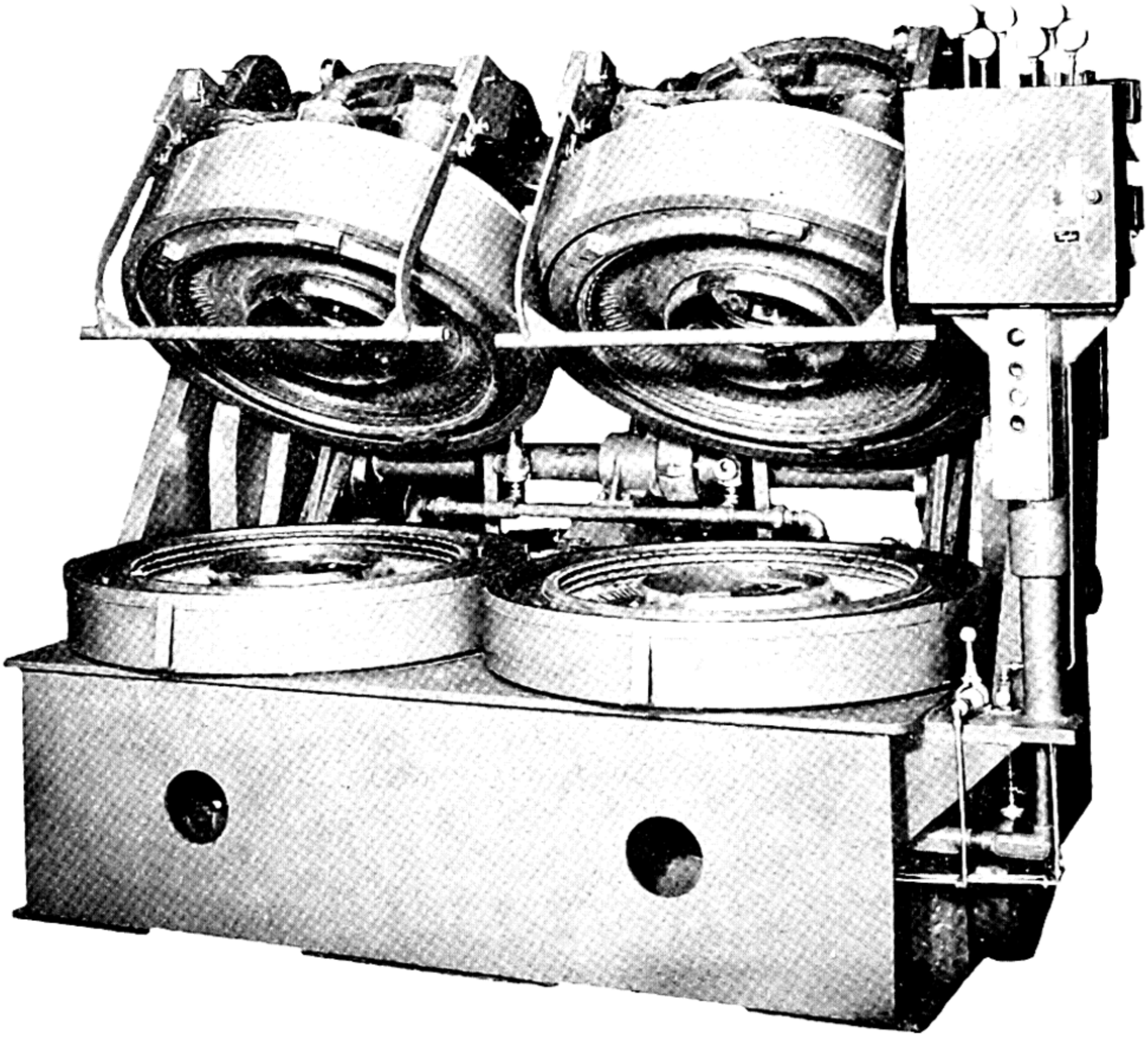


FIGURE 267.—A twin steam dome molding press, for curing automobile tires. The cast-iron mold itself is removable and replaceable. (Courtesy McNeil Machine and Engineering Company. Photo by Charles Mayer Studio, Akron, Ohio.)

first "dipped" in a bath containing either a latex-casein-"Dispersite" solution or a latex-resorcinol-formaldehyde solution, to enable the rubber to adhere firmly to the threads. It is then treated on the calenders as described for cotton fabric. Four-roll calenders are used to completely rubberize cord in one pass or operation at high speed.

Automobile tires and tubes. A high percentage of all rubber, whether natural or manufactured, is used in automobile tires and tubes. Tires are built up on a flat drum in successive plies of cord fabric, rubber-frictioned and coated, and cut on a bias angle of 50 to 60°. Cord fabric is composed of heavy twisted cords with very few light cross threads or none at all

(pickless). Pressure exerted by a stone in the road, for example, spreads the cords, but breaks nothing. Heavy tires have 6 or more plies, as well as heavy treads.

"Beads" of wire imbedded in hard rubber are attached to the edges of the fabric bands to give rigid anchorage to the rim of the wheel. "Flippers" and "chafing strips" used around the bead "tie-in" are of light square-woven fabric frictioned and coated with rubber. The top center of the carcass is protected by "breaker strips," and a slab of tough, abrasion-resisting stock which forms the tread. The sides are covered with thin rubber coatings, or "sidewalls."

Tires for trucks and buses in travel generate heat so rapidly that the temperature inside the tire may reach 280° F. (138° C.). As cotton has only half its normal strength at such temperatures, failure may occur. It was found that cord made of continuous rayon thread had far better resistance to heat, and that is the reason rayon cord ("Cordura") is used in large size tires for heavy vehicles to be operated at high speeds.

The tires just off the flat drum are shaped in a vacuum chamber after insertion of an "air-bag," a strong inner tube-like bag which has an air valve, and which will exert pressure on the inner side of the tire during vulcanization. The tire is placed in a two-piece, cast-iron or forged steel mold which has lettering, numerals and tread design in reverse. The mold is usually of the "watch-case" type, having a jacket through which it is heated by steam; however, it may be simply a movable mold, 18 or 20 of which are stacked on a hydraulic ram inside an upright cylindrical pressure vessel, where they can be heated by steam introduced around them. The watch-case type is being increasingly displaced by the "steam dome," consisting of an individual replaceable mold surrounded by a divided steam chamber mounted in a press. Steam and air, or steam and hot water, are introduced into the air-bag by flexible connections of copper tubing, expanding the tire carcass and causing the tread rubber, which is plastic at this stage, to flow into the desired design. The mold is heated for a specified time at a definite temperature, such as 40 minutes at 307°F. (153° C.) to produce vulcanization. The steam or other heating agent is then shut off, the internal pressure released, the mold opened, the air-bag removed, and the tire sent to final inspection. The tire shown in Figure 268 weighs 23 pounds and contains 12 pounds of rubber.

Tubular rubber in compounded form is extruded from a "tubing" machine, essentially a steel cylinder containing a close-fitting screw which forces the rubber stock fed at one end out through a die at the other end. Suitable lengths are now usually spliced mechanically before curing and cured in a "watch-case" mold on pressure applied through the valve. The cure is very short, usually about 6 minutes.

Rubber belting. Rubber belting is of much industrial importance, both for driving machinery and for conveying materials. Coated fabric is applied as shown in Figure 269, layers being added until the desired thickness is reached. On conveyor belts, a sheet of cover stock, properly compounded to resist abrasion or other service, is applied around the whole, and the belt cured in a flat or rotary press under hydraulic pressure totalling usually not

over 300 lbs. per sq. in. of belt in the press. Stretching devices are often used to keep the belt under tension during vulcanization.

Self-sealing fuel tanks. The great danger of a destructive fire when a bullet pierces the wall of an ordinary metal fuel tank led to the invention of the rubber self-sealing tank, installed on fighter planes and many others. One method of construction [16] is as follows: A plaster of paris form is covered with six layers of rubber and fabric; from the inside out, the layers are a GR-A lining, a rubber sealant, a rayon fabric, a second rubber sealant, a rayon fabric and the final outer layer, also rayon fabric which may be resin-impregnated. The sealant is $\frac{1}{8}$ to $\frac{3}{8}$ inch thick, and consists of unvulcanized synthetic rubber; when the bullet punctures the wall, gasoline reaches the sealant and swells it. In a short time (20 seconds) the swelling is sufficient to close the opening, and the tank is tight again. After the final layer has been applied, water is sprayed into the plaster form, and the weakened form is broken into pieces by mallet blows, and removed through the opening. The washed and dried tank is tested, and is ready for installation.

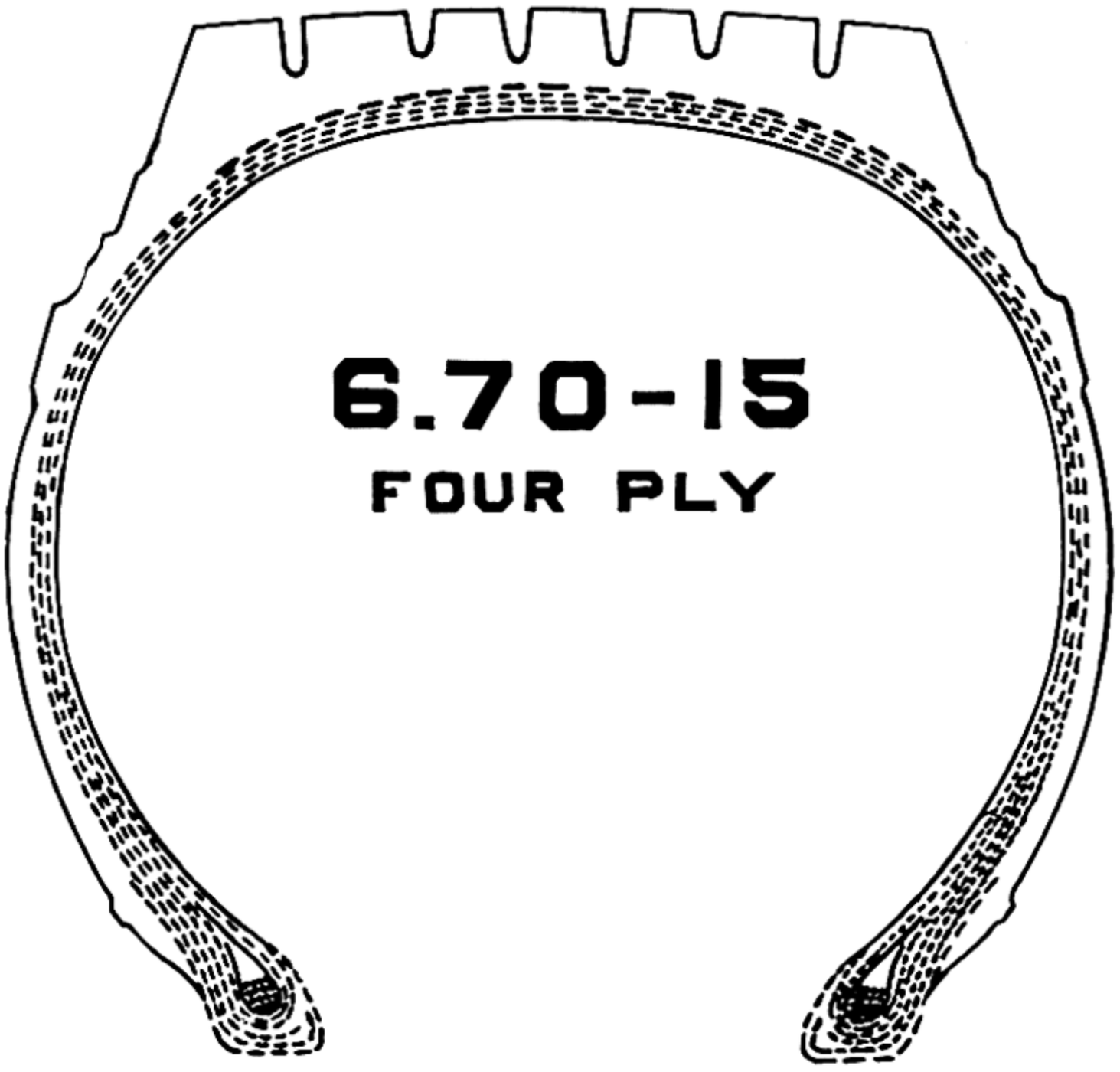


FIGURE 268.—A cross-section of the latest type of tire for passenger automobiles. At the top, note the tread, the non-skid grooves, the breaker strip under the tread. Down the side walls, the four strips are well shown, and at the bottom the bead wire, wrapped first in the flipper, then in the plies. (Special drawing for this edition prepared by courtesy of the Dunlop Tire and Rubber Company.)

The Mareng cell is also a rubber cell, not self-sealing, but with soft walls which fit themselves to whatever space they are to occupy. Still another useful fuel carrier is the disposable fuel cell, made of fiber board sprayed inside with "Perbunan," for example. It is dropped from the plane after use.

Garden hose and heels. Seamless tubing of compounded rubber is extruded, and then passed through the center of a loom which weaves on a covering of cotton threads. This, in turn, becomes the core for a second seamless rubber tube, a second cover of threads, and a final cover of seam-

[16] *Rubber Age*, p. 530 (Sept., 1943).

less tubing. The assembly then becomes the core for a seamless tube of lead, which is extruded by hydraulic pressure from a "lead press" carrying molten lead. The die through which the tube is passed is cooled so that the lead-covered hose emerges with the lead somewhat below its melting point. The hose is wound on a reel, placed in an autoclave, hydraulic pressure applied inside the hose, and steam introduced in the autoclave to produce vulcanization. Pressure is then released, the lead removed by a stripping machine, and the hose cut into lengths and couplings attached. "Pure gum" garden hose of synthetic rubber or other plastic, with no cotton inclusion, can be extruded and is being widely used; it can be made in attractive colors.

Stock for rubber heels is cut from sheets by means of a die, placed in molds and cured between steam-heated platens. The cure is usually about

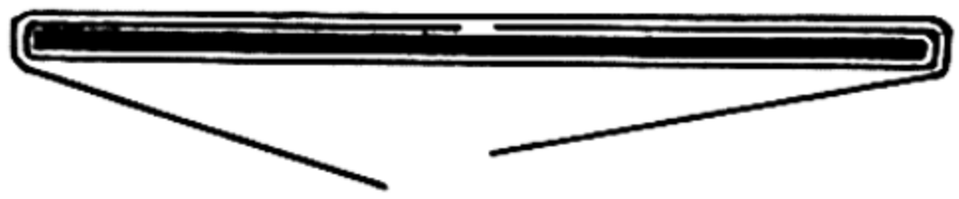


FIGURE 269.—Arrangement of canvas plies in a rubber belt for driving belts and conveyors (cross-section).

15 minutes at 307° F. (153° C.). Tan heels are colored with red iron oxide. Heel stock contains considerable filler so that the heel can be properly buffed. To give some idea of the volume of this item, one plant is said to turn out regularly 300,000 pairs of heels a day.

General. *Balata.* This is a gum of importance in the rubber industry, for it is used in combination with rubber for golf balls. The crude balata is purified by solution in naphtha, filtration, and evaporation, yielding the wax-like, nearly white gum.

Tennis balls are made by hot pressing and semicuring two hemispheres, cementing the two smoothed edges with a rubber cement, simultaneously introducing nitrogen under pressure, and sealing and curing the two hemispheres together. Two shaped pieces of felt are glued on for the covering.

Hard rubber. Rubber compounded with 30 to 50 per cent sulfur and then vulcanized becomes hard rubber. The time of cure is long, even with accelerators. Hard rubber has been partly displaced by synthetic plastics.

Cements and doughs. An unvulcanized rubber compound can be swelled with gasoline or benzol, and by successive addition of solvent and working in a mixer, converted into a viscous dough or cement. Such cements are used to unite rubber surfaces in preparation for vulcanization, and as adhesives for special uses.

Latex. Rubber latex itself is used in large quantities; it is shipped from the plantation to the consumer in drums, and even in tank steamers, after addition of ammonia to preserve and stabilize the emulsion. The raw latex is usually concentrated by creaming, by centrifuging, or by evaporating part of the water after addition of a stabilizer, or in a vacuum. Sulfur, accelerators, and other compounding ingredients may be added by using proper protective colloids.

Toy balloons, gloves and other thin objects are produced by dipping suitable forms in such compounded latex. Thus, to make the rubber gloves used for protection in acid plants, a porcelain form the shape of a hand is coated with calcium nitrate-glucose solution, and dipped into compounded latex.

A deposit forms in the exact shape of the hand; after it is thick enough, the form and glove are plunged into warm water for curing, after which the glove may be stripped off. The whole operation from beginning to end is a matter of minutes. By making the form the anode in an electrolyzing cell, thicker coatings may be formed (electrodeposition).

Sponge rubber. Sponge rubber is made by incorporating ammonium carbonate or stearic acid and sodium bicarbonate in a very soft rubber stock. The heat of vulcanization releases NH_3 and CO_2, which inflate the compound to a spongy mass, the size of the pores depending on the amount of gas, the softness of the stock and the rate of vulcanization. (See also Foam rubber, in this chapter.)

Butadiene Manufacture

From Ethyl Alcohol. During the war, large amounts of butadiene were manufactured from ethyl alcohol or ethanol, for use in the synthesis of GR-S. About one third of the rated capacity in the Government-sponsored plants was for butadiene from alcohol.[17] Ethyl alcohol was chosen partly because it offered an outlet for large volumes of alcohol made from grain, so that the farmer would be benefited; partly because it was thought that other source materials might not be abundant enough. Still another reason was that it was expected that the process could be put into operation more speedily than others, and this expectation was fulfilled. The first unit went into operation in January, 1943, about 10 months from the start of construction, and over a period to June, 1944, this process supplied more than 75 per cent of the total butadiene produced in Government-sponsored plants.

In the method [18] adopted after rapid yet intensive study, a portion of the ethanol is first converted to acetaldehyde, by dehydrogenation over a copper catalyst at a temperature above 250° C. (482° F.), at substantially atmospheric pressure. Next, ethanol and acetaldehyde are mixed in certain proportions, and reacted catalytically, with the formation of butadiene and water, as follows:

CH_3CH_2OH	+	CH_3CHO	→	$CH_2{=}CH{-}CH{=}CH_2$	+	$2H_2O$
ethanol (a liquid)		(volatile liquid) *acetaldehyde*		*1,3-butadiene* (a gas, forming a liquid under pressure)		*water*

The proportions are approximately 3 moles of ethanol to 1 mole of acetaldehyde. The reactor containing the catalyst is held at a temperature close to 325° C. (617° F.), and the pressure is near atmospheric, so that the reaction takes place in the vapor phase. The catalyst is silica gel impregnated with about 2.0 per cent of tantalum oxide (Ta_2O_5). There is a gradual decline in the activity of the catalyst, due to the deposition of carbonaceous matter, which must be burned off periodically (about every tenth day) in order to restore its activity. A series of reactors is available, so that the process will not be interrupted.

The products from the reactor are condensed, except for the ethylene and

[17] More exactly, 220,000 short tons per year, from alcohol; 622,500 tons total.

[18] "Production of butadiene from alcohol," W. J. Toussaint, J. T. Dunn and D. R Jackson, *Ind. Eng. Chem.*, 39, 120 (1947).

propylene gas, and separated by fractional distillation under pressure. The butadiene fraction contains 96 per cent of butadiene, and is refined by treatment with "Chlorex," and subsequent distillation. The resulting purity is at least 98.5 per cent. Excess alcohol is recovered and recycled.

In the preparation of acetaldehyde, the main product and the by-products, ethyl acetate and acetic acid are separated from the unreacted alcohol in the same system of distillation equipment as that used in the recovery of the products from the butadiene reaction.

An example representing the results in one month's operation of a unit in the plant gave the following figures: temperature 343° C. (649.5° F.); space velocity in liter fraction of liquid feed per hour per liter of catalyst, 0.37, equivalent to 2.8 gallons per hour per cubic foot of catalyst; molar ratio of ethanol to acetaldehyde in the feed, 2.75 to 1. The yield of butadiene was 63.9 per cent, which compares well with the average expected yield of 65 per cent; the other products were 8 per cent ethyl ether; 3.91 per cent ethylene; 3.97 per cent hexenes-hexadienes; 1.69 per cent propylene, and smaller percentages of some 20 other substances.

If the butadiene is to be shipped any distance, or kept in storage for more than a few hours, an inhibitor is added, which prevents spontaneous polymerization. Such a substance is tertiary butyl catechol. When such inhibited butadiene is about to be processed, it is stripped of its inhibitor by washing in caustic.

From Petroleum Refinery Products.[19] Of the sixteen butadiene manufacturing plants sponsored by the Government, three used alcohol as starting material, and thirteen used refinery products. Of the latter, six used butylene (generally 75 per cent) as the raw material for producing butadiene, and three started with butane, which was dehydrogenated to butylene in a preliminary step. Butadiene is made by the catalytic dehydrogenation of butylene, at elevated temperatures, so that there is great danger that the newly formed substance will combine with itself to form a polymer, to a major extent, thus giving low yields. It is necessary, therefore, either to work at low pressure, or to add a diluent which will reduce the partial pressure of the butylene to about 100 millimeters. It is imperative also, as in all dehydrogenation operations, to provide for extremely short contact times. Methane, another inert gas, or high-temperature steam may be used as diluent.

The latter process [20] was standard in at least seven of the Government-sponsored plants, and it has many advantages. It offers a convenient way to introduce the heat required by the highly endothermic reaction of dehydrogenation; for each pound of butylene converted, 725 B.t.u. must be supplied. The problem posed by the fact that all previously known dehydrogenation catalysts are deactivated by steam was solved by devising a new one, catalyst 1707; it consists largely of iron oxide (Fe_2O_3) on a magnesium oxide base with minor amounts of copper and potassium oxide.[21] The dehydrogenation of butylene takes place in reactors set up in pairs, so that one may be on

[19] With benefit of advice from Dr. C. E. Morrell, Associate Director, Chemical Division, Esso Laboratories, Standard Oil Development Company, Linden, N. J.
[20] *Tr. Am. Inst. Chem. Eng.*, 42, 1 (1946).
[21] U. S. Patents 2,395,875 and 2,418,888.

stream at all times. The reactors contain the catalyst in pellet form, on trays. A deposit of carbon forms during the reaction, and must be removed periodically. A great advantage of the steam dilution process is that steam alone (and no air) is sufficient to remove the deposit, because the water gas reaction takes place, consuming the carbon. While the catalyst in one reactor is being reactivated, the other reactor is on stream; reaction cycle and activation cycle are equal. The butylene conversion is 25 to 30 per cent. The vapors leaving the reactor are quenched and otherwise cooled, giving a condensate containing butadiene and unchanged butylene, from which a 98.5 per cent butadiene is produced in the butadiene recovery step. This last operation presented difficulties which were solved by the introduction of extractive distillation with furfural, or by other means.

Some further information on the steam dilution process follows. The reactors are 16 feet internal diameter, and the height is sufficient to permit a single fixed bed of catalyst pellets as high as 72 inches. The operating temperature range is from 1150 to 1250° F. (621 to 677° C.); the reactor outlet pressure is atmospheric. The cycle is 2 hours. The depth of the catalyst bed was reduced from an original 72 inches to 60, and later to 42 inches, which gave higher space velocities. The superficial reactant residence time is about 0.2 second. By feeding in and restoring constantly a component of the catalyst which is gradually lost, high activity of the catalytic mass is maintained, and a conversion of 30 per cent is reached, with runs lasting up to six months. The hot reactor effluent is quenched with a pumped stream of condensate, passes to a waste heat boiler, and then to other quench towers. The liquid condensate, separated from water, is stabilized in a fractionator, then divided in a rerun tower into an overhead containing the butadiene with other C_4 hydrocarbons, and a polymer bottoms stream. The crude butadiene is sent to the butadiene recovery area, where unreacted butylene is also recovered. For each pound of butylene consumed, 0.61 and even 0.64 pound of butadiene in the finished state is obtained.

For the production of 98 per cent butadiene from fractions containing a lower percentage, several methods have been devised. The difficulty lies in the slight differences in the boiling points of the components of the butadiene-containing fraction coming, for example, from the butylene process; it is essentially a mixture of C_4 hydrocarbons. Similar considerations obtain when streams from other refinery operations, but with a butadiene content, must be worked up. The several methods are: extractive distillation with furfural; azeotropic distillation with ammonia; solvent extraction with ammoniacal cuprous acetate.

In *extractive distillation*,[22] a foreign substance is added which is relatively non-volatile, as compared to the hydrocarbon mixture being separated, and which modifies the volatility of the chemical bodies present, in different degrees, so that separations which were not otherwise possible, or not practical, become possible. The effect of the added substance, furfural, on the C_4 hydrocarbons concerned in this study, is shown in Table 145.

[22] *Trans. Am. Inst. Chem. Eng.*, **42**, 189 (1946).

TABLE 145.—*Relative volatility*[23] *(most volatile at top, least volatile at bottom).*

Normal	Over furfural
Isobutane	Isobutane
Isobutene	*n*-Butane
Butene-1	Isobutene
Butadiene	Butene-1
n-Butane	*trans*-Butene-2
trans-Butene-2	*cis*-Butene-2
cis-Butene-2	Butadiene

[23] *Ibid.*, p. 193.

In the butadiene fraction from butylene dehydrogenation, most of the butene-2 is removed by straight distillation, as bottoms, while the overhead, consisting of butadiene and butene-1, goes to the butadiene solvent tower. Here, in the presence of furfural, the overhead is butene-1, which is rejected, while the bottoms are the solvent rich in butadiene. The hydrocarbons are stripped from the solvent, and then redistilled to give 98.5 per cent butadiene overhead, with some butene-2 in the bottom flow. All hydrocarbons separated from the butadiene are utilized elsewhere in the refinery. Separation by straight distillation of *n*-butane (32° F.; 0° C.) from *trans*-butene-2 (33.8° F.; 1° C.) would be very difficult; but in the presence of furfural, which raises the volatility of the first more than that of the second, it is simple, the *n*-butane coming out as overhead. Another extractive distillation permits the separation of isobutane from butene-1, and still another example is the separation of a small percentage of *n*-butane from butadiene.[24]

The separation of butadiene by azeotropic distillation with ammonia is performed in fractionating columns working at 215 lb./sq. in. The method was applied successfully in one of the earlier, smaller plants.[25]

In the cuprous salt solution method,[26] which has been applied in plants producing 55 per cent of the total Government-sponsored production, a cuprous ammoniacal acetate solution (CAA) absorbs the butadiene in dissolved form, and at a later stage releases it in concentrated form. The process may be run in two different ways: with the hydrocarbons in the gas phase contacting the solvent in packed towers, or with liquid-liquid contact. In the gas phase method (three-stage), there are three main operations.

In the butadiene absorption tower, crude butadiene in vapor form enters at the base of the packed tower, while the copper solution enters at the top and travels down. The butadiene dissolves, with a consequent rise in the viscosity of the solution. Unabsorbed hydrocarbons pass out overhead. The solution enters the second tower, where by means of a reduction in pressure, unsaturated hydrocarbons other than butadiene are released, causing butadiene enrichment. The third step is the desorption of the butadiene solution, which issues from the base of the enrichment tower; it enters the desorption tower near the top, where by means of moderate heat, the butadiene is released, and passes out in vapor form overhead. The butadiene

[24] *Ibid.*, 42, 1002 (1946).
[25] *Ibid.*, 815 (1946).
[26] *Ibid.*, 473 (1946).

vapor is condensed and distilled, to recover ammonia. All three towers are packed.

Operation by the liquid-liquid contact method (in packed towers for the absorption phase) proved very satisfactory, so much so that the processes yielding most of the butadiene made employ it in both the absorption and enrichment stages. In the former, some refrigeration is required; in the enriching and desorption steps, where heat is required, low-pressure steam in moderate amounts is sufficient.

The stocks fed to concentration processes contain 15 to 35 per cent of butadiene.

A list of 14 unsaturated hydrocarbon compounds which may occur in crude butadiene fractions is on record.[27] Included are acetylene derivatives which are eliminated from the product largely by selective desorption from the solvent and by polymerization to materials boiling higher than the butadiene product.

STYRENE[28]

About 90 per cent of the styrene consumed in the manufacture of GR-S during the war was produced by the Dow process, namely by the catalytic dehydrogenation of ethylbenzene, itself formed by the alkylation of benzene by anhydrous aluminum chloride.[29] The alkylation reaction is:

$$\underset{\substack{\textit{benzene}\\(\text{a liquid})}}{C_6H_6} + \underset{\substack{\textit{ethylene}\\(\text{a gas})}}{C_2H_4} \xrightarrow[AlCl_3]{95^\circ\ C.} \underset{\substack{\textit{ethylbenzene}\\(\text{a liquid})}}{C_6H_5\cdot C_2H_5} \qquad (1)$$

The dehydrogenation reaction is:

$$C_6H_5\cdot C_2H_5 \underset{\text{Catalyst}}{\overset{630^\circ\ C.}{\rightleftharpoons}} \underset{\substack{\textit{styrene}\\(\text{a liquid})}}{C_6H_5\cdot CH{=}CH_2} + H_2 \qquad (2)$$

A complete train of units consists of an ethylbenzene block, a dehydrogenation block and a styrene finishing block. In the alkylation step, benzene and ethylene are reacted in the presence of aluminum chloride and some ethyl chloride; the latter serves as the source of hydrogen chloride desired as a promoter. The reactor is a vertical cylindrical vessel, lined with acid-resisting bricks, containing the liquid reaction mixture to a depth of 34 feet. The ethylene bubbles in at the bottom, and provides circulation of the liquid as it rises. The reaction is exothermic. To maintain the temperature at 95° C. (203° F.) it is necessary to cool; this is done by an overhead condenser and a curtain of cold water flowing down the outside of the shell. The pressure in the reactor is 5 lb./sq. in. or less. In addition to ethylbenzene, polyethylbenzenes are formed, which are undesirable. To minimize

[27] *Ibid.*, 476 (1946).

[28] With benefit of review by Mr. J. E. Mitchell, Assistant Manager, Plastics Division, The Dow Chemical Company, Midland, Michigan.

[29] "The Dow process for styrene production," J. E. Mitchell, Jr., *Trans. Am. Inst. Chem. Eng.*, 42, 293 (1946); see also "Los Angeles styrene plant," H. H. Smith, *Chem. Eng. Prog.*, 43, 152 (1947).

the amount formed, an excess of benzene is maintained, and a certain amount of polyethylbenzene is recirculated. The ethylene-to-benzene ratio is, for example, 0.58 mole of the former to 1.00 mole of the latter. Polyethylene introduced into the reactor is partly dealkylated to ethylbenzene. To maintain the required anhydrous state, both the new and the recovered benzene are dehydrated by azeotropic distillation. The feed of dry benzene and fresh aluminum chloride, the bubbling in of ethylene, and the withdrawal of reaction mixture are continuous.

The crude ethylbenzene withdrawn is cooled, decanted from a lower layer consisting of aluminum complex hydrocarbon compounds (twice), then mixed in an oversize pump, which acts as contactor, with a solution of 10 per cent caustic soda. The decanted ethylbenzene is fed to a stripping column, which gives overhead ethylbenzene and benzene, and at the bottom heavier materials which pass to the polyethyl still. The overhead in vapor form enters the benzene still, which gives a bottoms ethylbenzene and higher-boiling hydrocarbons. It is distilled once more, then washed with 20 per cent caustic soda solution, and dried by passing through a bed of flake caustic. Its purity is 99.5 per cent. Recovered benzene is recycled.

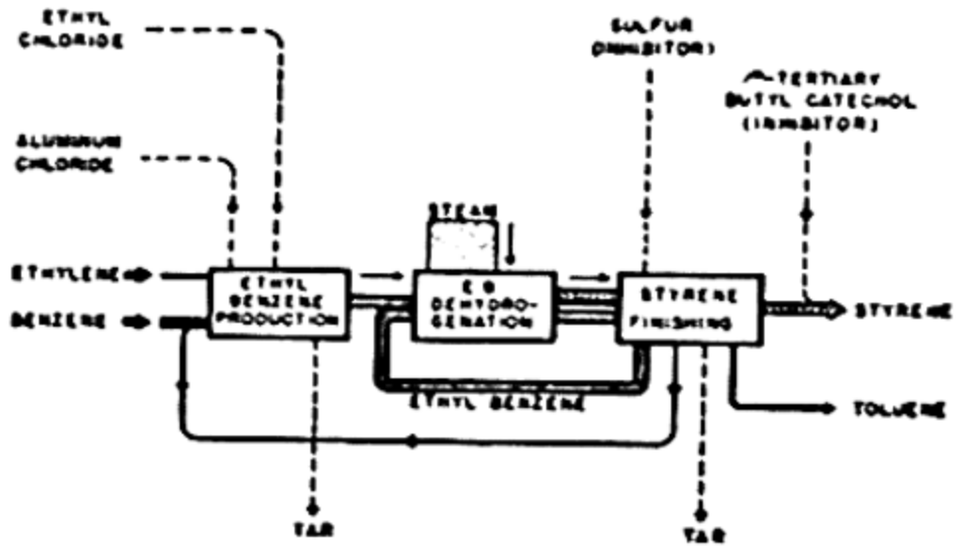


FIGURE 270.—A simplified flow diagram for the production of styrene from benzene and ethylene, which also indicates the relative flow quantities. (From *Trans. Am. Inst. Chem. Eng.*, 42, 294, by permission.)

The second step—dehydrogenation of ethylbenzene to styrene—is an endothermic reaction run in the presence of superheated steam, which acts as an inert gas diluent. A solid catalyst is used in this reaction. The theoretical reaction (2), without modifying or diluting agents, has an equilibrium which would give, at 630° C. (1166° F.), 25 to 30 per cent styrene in the liquid product, which is a low yield. Inasmuch as the reaction from left to right runs with an increase in volume, a decrease in the partial pressure of the products would favor it. Working under reduced pressure is impractical, but the same result is obtained by the introduction of a suitable inert gas in the ratio of 2.6 lbs. of steam to 1 lb. of ethylbenzene. This reduces the partial pressure of the reaction products to 0.1 atmosphere, and shifts the equilibrium so that a theoretical styrene concentration of 70 to 80 per cent in the liquid product is possible. The superheated steam has two other functions: it supplies the needed reaction heat, and it keeps the catalyst clean by reacting with deposited carbon. The catalyst raises the reaction rate for this same temperature to a satisfactory one, with a minimum of side reactions.

The reactor consists of an insulated brick chamber containing the catalyst in granule form. The catalyst (formerly known as 1707), developed for the

dehydrogenation of butylene in the presence of steam, and described earlier in this chapter, was found to do well in the present process, and was used extensively over the war period for this purpose. About 90 per cent of the steam is raised to 383° C. (725° F.) by heat exchange with product vapors, then to 710° C. (1310° F.) in a superheating furnace. The balance of the steam is mixed with the ethylbenzene charge at 160° C. (320° F.) and raised to 520° C. (968° F.) by heat exchange with product vapors (ahead of the steam). The two streams meet in concentric inlet tubes and, thoroughly mixed, enter the catalyst chamber (Figure 271). The reactor is held at 630° C. (1166° F.) (at the base). The outgoing vapors are cooled by heat exchange, followed by a spray-type desuperheater, and a final condenser.

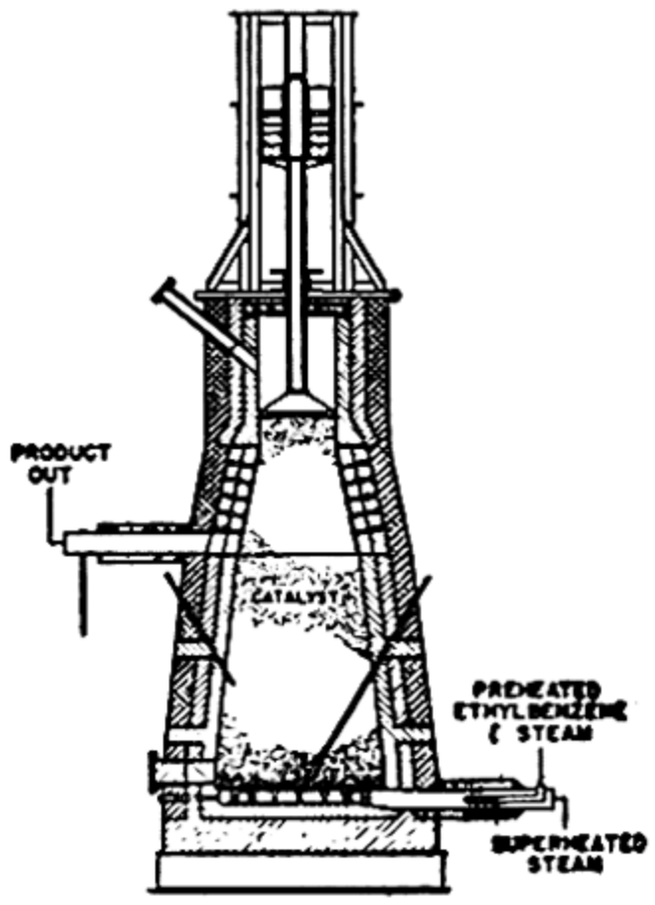


FIGURE 271.—The catalytic reactor for the dehydrogenation of ethylbenzene. (From *Trans. Am. Inst. Chem. Eng.*, 42, 302, by permission.)

The condensate is steam, ethylbenzene, styrene, benzene, toluene and tar. The conversion is approximately 37 per cent [fresh catalyst, and 600° C. (1112° F.)]. Vent gas contains hydrogen, carbon monoxide, carbon dioxide, methane, and others. The life of the catalyst with uninterrupted operation is a year or more.

In the styrene finishing step, pure styrene is isolated from the crude condensate, containing approximately 37 per cent styrene, by distillation at reduced pressure, in the presence of elemental sulfur as a polymerization inhibitor. The small differential in boiling points between ethylbenzene [136.2° C. (277° F.)] and styrene [145° C. (293.4° F.)] makes it necessary to employ a 70-plate tower, in the form of a 38-plate and a 32-plate tower, working in series. The bottoms are the styrene; they pass to two batch-finishing stills with packed towers (operated under vacuum), where the styrene is the overhead; tar and sulfur are left behind. The product styrene, 99.7 per cent pure, is cooled and refrigerated, after addition of 10 to 15 p.p.m. of TBC (para-tertiary-butyl catechol) as inhibitor, and shipped in insulated tank cars.

In a preliminary distillation at reduced pressure, with sulfur present, benzene and toluene have been removed. The benzene is recycled to the ethylbenzene block. Toluene is a by-product. The overall yield, benzene to styrene, is 88 to 92 per cent; ethylene to styrene, the same.

Other Patents

U. S. Pat. 1,755,891, dispersing coagulated bodies by introducing clay, mixing, and removing the clay by addition of water (W. B. Pratt); dispersing by means of a solvent, 1,621,468; by means of glue and saponin, 1,732,027; by means of a colloidal substance, 1,731,725; 1,874,546, coagulation of latex emulsion; 1,885,154, process to produce a concentrated and purified rubber latex; 1,850,673, reducing the alkalinity of latex by treating with silica gel; 1,804,157, a creaming agent for latex; 2,029,410, on chemical products and producing same (Neoprene) to Wallace H. Carothers, Arnold M. Collins, James E. Kirby, with 30 examples, 25 claims; 2,002,622, on stabilizing latex; 2,279,293, on a new synthetic rubber from butadiene and isobutyl acrylate; 2,451,787, emulsion polymerization of chloroprene.

Problems

1. In the analysis of a rubber compound, the rubber is first treated with acetone in order to remove or extract the "free" sulfur, and then the sulfur which is "combined" with the rubber, or one of the admixtures, is determined in the residue by combustion for example, or by oxidation, leading in either case to a precipitation in the form of barium sulfate. In a sample under study, the acetone extract is found to give 5.4 per cent free sulfur on the weight of the sample. The extracted sample is shown to have 3.1 per cent sulfur based on the weight of the extracted sample.

(a) What is the percentage of "combined sulfur" in the original sample? (b) What is the percentage of the "combined sulfur" if the original sample contained 5.0 per cent lithopone (29.0 per cent ZnS, 71.0 per cent $BaSO_4$)? Note: $BaSO_4$ in the lithopone is filtered off along with any insoluble residue after oxidation, while the ZnS is dissolved.

Reading References

"The preparation and properties of GR-S," Frank J. Soday, *Trans. Am. Inst. Chem. Eng.*, 42, 647 (1946).

"Plastication and processing of GR-S," George R. Vila, *Ind. Eng. Chem.*, 36, 1113 (1944).

"Production of butadiene from alcohol," W. J. Toussaint, J. T. Dunn, and D. R. Jackson, *Ind. Eng. Chem.*, 39, 120 (1947).

"Deoxygenation of certain aldehydes and ketones: Preparation of butadiene and styrene," W. M. Quattlebaum, W. J. Toussaint and J. T. Dunn, *J. Am. Chem. Soc.*, 69, 593 (1947).

"The production of butadiene by the dehydrogenation of normal butylenes," R. P. Rusell, E. V. Murphree and W. C. Asbury, *Trans. Am. Inst. Chem. Eng.*, 42, 1-14 (1946).

"Purification of butadiene with cuprous salt solutions," C. E. Morrell, W. J. Paltz, W. C. Asbury and C. L. Brown, *Ibid.*, 42, 473 (1946).

"Separation of butadiene by azeotropic distillation with ammonia," N. Poffenberger, L. H. Horsley, H. S. Nutting and E. C. Britton, *Ibid.*, 42, 815 (1946).

"Butane dehydrogenation by the Houdry process," R. C. Lassiat and F. D. Parker, *Petr. Ref.*, 23, 409 (1944).

"Ethylbenzene synthesis from benzene and ethylene with phosphoric acid catalyst," W. J. Mattox, *Trans. Am. Inst. Chem. Eng.*, 41, 463 (1945).

"Los Angeles styrene plant," H. H. Smith, *Chem. Eng. Prog.*, 43, 152 (1947).

"Styrene production by catalytic dehydrogenation. Low-pressure operation," J. M. Mavity, E. E. Zetterholm, and G. Hervert, *Trans. Am. Inst. Chem. Eng.*, 41, 519 (1945).

"Extractive distillation. Separation of C_4 hydrocarbons using furfural," J. Happel, P. W. Cornell, DuB. Eastman, M. J. Fowle, C. A. Porter, and A. H. Schutte, *Ibid.*, 42, 189 (1946) and a discussion, same volume, p. 1001.

"The Dow process for styrene production," J. E. Mitchell, Jr., *Ibid.*, 42, 293 (1946).

"Process design of catalytic reactors. Dehydrogenation of butane," R. H. Dodd and K. M. Watson, *Ibid.*, 42, 263 (1946).

"Hypersorption process for separation of light gases," Clyde Berg, *Ibid.*, 42, 665 (1946).

"Constitution of polysulfide rubbers," S. M. Martin, Jr., and J. C. Patrick, *Ind. Eng. Chem.*, 32, 1144 (1936).

"Formation of high polymers by condensation between metallic polysulphides and dihalogenated hydrocarbons and ethers," J. C. Patrick, *Trans. Faraday Soc.*, 32, 347 (1936).

"Manufacture of Thiokol," T. F. Harragan, *India Rubber World*, 95, No. 3, 38 (1936).

"Continuous isolation of GR-M from Latex," M. A. Youker, *Chem. Eng. Prog.*, 43, 391 (1947).

"Low-temperature manufacture of chemical rubber," W. H. Shearon, Jr., J. P. McKenzie and M. E. Samuels, *Ind. Eng. Chem.*, 40, 769 (1948).

"Domestic natural rubbers," F. E. Clark, *Chem. Eng. News*, 26, 926 (1948).

A correct appraisal of what advantage may be derived from the patent laws, and a knowledge of their dangers and limitations, are an essential part of the education of the future chemical engineer and industrial chemist.

Chapter 40

Patents

A patent is a publication, a disclosure, for the benefit of the public, and of posterity.

A patent is granted by a government in consideration of the disclosure of a means or method which may be applied to practical use. The purpose of issuing patents is to encourage the development of the practical arts. Inventions disclosed by patents are for the ultimate benefit of the public. As an inducement for creating inventions, and for divulging their secrets, the law offers the inventor a monopoly for a limited period.

This may be a doubtful gift, since the burden of enforcing this monopoly is carried by the patentee, and infringement on the inventor's patent must first be discovered by him, and unless the infringer settles or ceases his infringement, suit must be brought in the Federal courts and prosecuted by the inventor. The law is passive; if the patentee succeeds in proving the charge of infringement, the courts will grant an injunction during the life of the patent and award damages and profits. Frequently it is difficult to prove that there is an infringement, particularly for the chemist patentee, since usually chemical plants are closed to public inspection. However, if there are substantial grounds for believing that there is a case of infringement, the courts will compel the alleged infringer to disclose fully. If the patent is on a chemical product which can be made in only one way, the problem is simpler; but such articles are few. As a rule, the products are well known and can be made in a number of ways, so that the mere selling of the product proves nothing. The infringement of a patented automobile device is comparatively easy to determine, since the invention must appear on the public highways; similarly a new and improved type of cardboard box, suitable for an egg container, necessarily must appear in public, and the question of infringement is comparatively simple to determine. This may not be true with the average chemical patent; the infringer may hide behind factory walls; the article put on sale may reveal nothing as to its method of manufacture. For this reason, not infrequently chemical processes have been kept secret.

Keeping a process secret, however, also involves risk; an unfaithful employee or partner may take out a patent on such process and force the original discoverer to pay tribute on his own discovery. This may seem a harsh rule of law, but the fundamental principle of the patent law is that inventive discovery shall be made public for the benefit of everyone, and he who chooses to keep the invention secret must do so at his own risk. A monopoly based on a secret process is unsafe, unless the secret is so thoroughly guarded as to substantially preclude the possibility of outside parties learning it.

It goes without saying that no reputable business house will consciously infringe, but will gladly give to inventive ability due recognition and reward. The danger of loss of the monopoly comes from the acts of individuals and corporations in business whose policy is determined by greed rather than principle.

The patent law is rooted in the Federal Constitution and is defined by Congressional statutes.[1] Its purpose is to obtain for the benefit of the public valuable information which will advance the practical sciences and arts, which otherwise might be lost on the death of the inventor. The law is primarily good for the public and, for a limited period, protects the inventor.

Statutory Classes of Invention

The patent statute divides patentable subject matter into four classes: viz., arts, machines, manufactures, and compositions of matter.

1. The word "art" in the statute includes the substantially synonymous terms "process," "mode," and "method." This term includes an act or a series of acts which may be carried out, by hand or otherwise, without reference to any special mechanism, such as the art of dyeing or steel making. The mere function of a machine cannot be patented as an art or process. It is under the heading of an art, method, or process that many chemical patents are granted, although some are granted as compositions of matter.

2. A "machine" is usually a combination of mechanical parts which are adapted to receive, transmit, and modify force or motion to do useful work.

3. The term "manufacture" covers articles or fabric made as finalities and thereby distinguished from machines by not having any rule of action, and from compositions of matter by not involving the relation of ingredients. Examples are a chain, a lamp, or a chimney.

4. A "composition of matter" is a compound of two or more ingredients forming a homogeneous whole, such as paint, glue, ink, or a dye.

Patentability

The subject matter of a patent must involve invention; it must be new; and it must be useful.

(*a*) The question as to whether a creation is an invention is largely a question of fact. No court has been able to give a general positive definition of this term as used in the patent law. Many rules have been made for testing the question of invention, substantially all of which are negative, but they nevertheless serve as guides in most cases as well as positive rules. Some of such rules are:

1. Mere mechanical skill is not invention.

2. Excellence of workmanship is not invention.

3. Usually the substitution of one material for another is not invention; thus if wood is replaced by aluminum, a phenol-formaldehyde plastic, or iron, this does not constitute an invention, unless such substitution produces some new and unexpected results.

4. A change of size is not invention.

5. A change in degree or form is not invention.

6. An aggregation of parts which does not interdependently co-operate to produce a useful result is not an invention; thus the courts have held that a rubber-tipped

[1] Article 1, Section 8; the Patent Office was established by Act of Congress in 1790; the first patent was a chemical one, for a process for making potash and pearl ashes (U. S. Patent 1, to Samuel Hopkins, July 31, 1790).

lead pencil cannot be patented, since the lead and the rubber are not simultaneously used.

7. Mere duplication of parts is not invention.

8. The omission of an element is not invention.

9. The substitution of an equivalent is not invention. The breadth of patent claims depends largely upon the interpretation of equivalents. In general, it may be said that a basic or pioneer invention will have a much greater range of equivalents than an invention making only a small advance in an established art.

10. Using an old thing for a new and analogous purpose is not invention.

In a decision made in 1941, the United States Supreme Court held "that the test of patentability is whether a 'flash of creative genius' is revealed by the alleged invention. The High court proclaimed that, unless a strict application of this test reveals the presence of such a flash, a patent is invalid for want of invention."[2] This important and perhaps disturbing decision has caused much discussion.[3] It is at least a positive statement regarding what constitutes invention. If it is interpreted reasonably, many more patents would be ruled valid today than may seem at first sight. Several other means of evaluating this quality have been used by the courts in the past; there has been deemed to have been invention when (1) the result was unexpected; (2) long experimentation had been required; (3) the last step, until then vainly sought by others, was taken, which turned all the previous steps into a success; there are still others.

(*b*) An invention must be new. This means that the invention must not have been the subject of publication anywhere in the world prior to the date of invention here, and must not have been in use in the United States of America prior to such date of invention. Foreign patents are called publications. Therefore, no valid United States patent can be granted for any invention described in patents issued in foreign countries.

Novelty is not negatived by abandoned experiments; if experiments have been performed, and then dropped, even though partially or accidentally performing the function desired, such experiments will not anticipate a later perfected invention. If, however, such experiments are completed and a patent application is filed in the Patent Office within two years after the first public use, a valid patent may be secured.

Prior accidental production is not an anticipation and does not destroy novelty.

The prior use of an invention in countries foreign to the United States is not an anticipation; but a prior domestic use is an anticipation.

(*c*) The invention must be useful in the industrial arts. This limitation automatically rules out many freak inventions which would consume the time of the examiners and give nothing of value to the public. An inoperative combination or process, which will not answer the purpose for which it was intended without redesign or alteration, is not an invention.

A scientific principle cannot be patented; a useful application of it to the industrial arts must be presented. Likewise the principle or function of a machine cannot be patented.

[2] Quoted from the article "Flash of Genius"—"Patent doctrine and the chemist," by Thomas Cifelli, Jr., *Chemical and Engineering News*, 20, 523 (1942).

[3] "Patent litigation in 1940 and 1941," by Nelson Littell, *Ind. Eng. Chem.*, 34, 88 (1942).

Patent Applications. All patent applications must be filed with the Commissioner of Patents at the Patent Office,[4] Washington, D. C. A preamble recites the object of the invention; this is followed by a description of the invention, which must be full, clear, concise, and exact enough to enable any person skilled in the art or science to which it pertains or to which it is connected most closely to make and use the invention. If it is a machine, the description must be exact enough to enable its manufacture; if it is a composition of matter, the description must be clear enough to permit the compounding; if the invention is a process, the method of carrying it out must be clearly described.

The claims follow the description and point out the novelty of the invention. For each novel part, a distinct and formal claim is necessary, since patents are not granted except for those novel disclosures which are distinctly claimed. The monopoly granted is limited to the contents of the claims.

The application is accompanied by an oath made by the inventor, setting forth that he is the sole inventor (or if more than one, that they are the sole joint inventors), that he does not know and does not believe that his invention was ever known before his discovery thereof, or patented or described in any printed publication in any country before his discovery thereof, or more than two years prior to his application, or in public use or on sale in the United States for more than two years prior to his application; and further that his invention has not been patented in any country foreign to the United States on an application filed by him or on his authority more than twelve months prior to his application.

Whenever drawings will make the disclosure clearer, they must be presented with the application. In former years, models were required, but they are not any longer.

The fee due on the patent application is $30 when filed, and the final fee for issuing the patent is $30. The fees for design patents vary according to their term.

Patent Office Actions. On receipt at the Patent Office, an application is given a serial number and then goes to one of about fifty different divisions, each one of which handles a single group or a series of related groups of inventions. Each of these divisions is supplied with copies of all domestic and foreign patents and most of the publications on the subjects handled in that division. Each division has one head or principal examiner, and a number of primary or assistant examiners. If the application is rejected because of prior publication or technical defects in the form of the application, a letter of rejection is returned to the applicant or his attorney, setting forth succinctly the reasons for rejection. The applicant or his attorney must secure copies of all references cited by the examiner, and he has six months from the date of the office action in which to amend his application, or point out to the examiner the differences between the disclosures of the publications referred to and his own invention. The wording of his original application may be changed by amendment, but the applicant is not permitted to add any new matter. If the application is twice rejected

[4] Since 1925, part of the Department of Commerce.

on the same grounds, such rejection is made final; the applicant may then appeal to the Board of Examiners-in-chief of the Patent Office; from this board, he may appeal to the Commissioner of Patents; from the Commissioner's decision, he may appeal to the Circuit Court of Appeals of the District of Columbia. The decision of the last-named court controls the action of the Patent Office on the matter at issue.[5]

Interferences. It sometimes happens that two patent applications for substantially the same invention are pending in the Patent Office at the same time. An interference is a proceeding instituted for the purpose of determining the question of priority of invention between two or more parties claiming substantially the same patentable invention. Patents are granted to the first inventor. The fact that one of the parties to an interference proceeding has already obtained a patent will not prevent an interference, for, although the Commissioner has no power to cancel the patent, he may grant another patent for the same invention to the person who proves to be the prior inventor. The first inventor to file his application in the Patent Office is the senior party to the interference. The burden of proving the date of invention is upon the party who last files his application. If he succeeds in overcoming the date of the filing of the first party's application, then the burden of proving priority of invention shifts to the party first filing. Priority is determined by proof of a series of facts, such as:

(*a*) the date of the conception of the invention;
(*b*) the date of the disclosure of the invention to another person;
(*c*) the date of the first drawings, if any;
(*d*) the date of the first model, if any;
(*e*) the date of the first reduction to practice, such as the commercial operation of the invention; the date of filing a patent application is in the patent law a constructive reduction to practice.

The importance of keeping properly dated memorandum books, or notebooks, or other proof concerning the invention will at once be apparent to the young chemist.[6]

If there are no rejections, or if the rejections have been overcome, and

[5] A bill to establish a Court of Patent Appeals was introduced in the United States senate in January, 1937, by Senator McAdoo. The court would have exclusive appellate jurisdiction to review by appeal final decisions of the district courts; it would have three permanent scientific advisers.

[6] The United States Department of Agriculture had filed suit (in March, 1932), with the United States Court of Customs and Patent Appeals, contesting the validity of U. S. Patents 1,787,416 and 7, granted to Alfred Wohl, of Germany. The patent 1,285,117 issued to Gibbs and Conover in November, 1918, had been cancelled by the Court of Appeals at the time the Wohl patents were issued. The question of the date of "reduction to practice" in the case of each invention became the determining factor. The date for Gibbs-Conover is September 7th, 1916; for Wohl, either September 4th or 9th, 1916, depending upon the interpretation of "reduction to practice" by the court. In March, 1934, the court awarded priority to Wohl, and declared the Wohl patents valid. The original application to the German Patent Office by Wohl, of June 28th, 1916, was amended by him on September 4th and again on the 9th, 1916, listing the higher temperature, 350 to 550° C., which had been also stated by Gibbs. The court decided that Wohl was entitled to a date for reduction to practice at least as early as the date of the filing of his amendment. Nothing solid earlier than September 4th could be shown by Gibbs and Conover. This case brings out the importance of the availability of proofs of date and hour of "reduction to practice."

if no interferences have been found, the applicant is notified that his patent will be allowed; he is then given an interval of six months within which to pay the final fee for issuing the patent. All patents are issued on Tuesdays. If the final fees are paid on or before a Thursday, the patent will be issued on the fourth Tuesday thereafter.

Searches. Much information as to the advisability of patenting an invention may be obtained by means of preliminary searches. Such searches may be made for the purpose of determining in advance the patentability or the validity of proposed claims, or whether the invention would infringe prior patents if commercially exploited. These searches are never performed by the Patent Office until after the patent application is filed, but they may be obtained through attorneys who are skilled in this work. In the Patent Office all domestic and foreign patents are classified according to their subject matter. There is no other place where such a classification can be found. It is, therefore, essential that such searches be made in the Patent Office by those who are familiar with the classification.

Patentability searches are made to determine whether an invention is novel and patentable. Such searches are made among the issued patents, and reports upon them are usually accompanied by a few selected copies of the patents closest to the invention searched. Such a search determines the advisability or inadvisability of filing a patent application. The cost of such searches varies from $5 up. The search made by the inventor through complete files of patents usually wastes much time and is inconclusive, since the files of patents in the libraries are not classified and many pertinent patents may be overlooked.

A determination of whether the invention has been in public commercial use is difficult to make. The knowledge of the commercial men of the art is frequently valuable in determining this question, but sometimes a restricted public use may have been made and not be known to those familiar with the general trade. If the invention has been in public use, even though such use is restricted, for more than two years, it will invalidate any patent granted on the invention.

Validity and infringement searches cover substantially all of the patents which come within the scope of the invention in question and are made in order to determine, as positively as can be done, whether the proposed patent, if granted, would be valid, and the invention, if commercially made, would infringe prior patents. Such validity and infringement searches are usually quite expensive and frequently cost several hundred dollars. It should be noted that the Patent Office merely determines the question of novelty and does not attempt to determine the question of possible infringements of prior patents; the grant of a patent does not guarantee the inventor that his invention is free from the dominating influence of a prior patent. In expensive commercial operations, therefore, validity and infringing searches are quite important.

Title. The monopoly granted by the patent belongs to the inventor; it is property and the title is vested in him. Such title is absolute and unqualified; the Federal Government cannot take it away from him; the State cannot interfere. Only a court in bankruptcy can pass title to a patent

without the written consent of the patentee; a receiver in a State court may administer a patent but cannot transfer the title.

The monopoly granted by the patent is legally transferable. The patentee himself may pass title to any other person or to a corporation, but he must do so by means of a written assignment. In order that an assignment shall be legally effective against a claim by strangers who did not know of such assignment, it must be recorded in the Patent Office within three months after its date. If such record is not made within the time stated, a subsequent assignee, not knowing of the first assignment, may secure a valid title to the patented invention, if he complies with the law by recording his subsequent assignment, and, in that event, the only remedy of the first assignee is to sue the assignor for fraud.

The patentee, if he pleases, may refrain from making, using, or selling his invention and may decline to permit others to do so. The patentee may retain title to his patent, and grant licenses to operate and sell or use the invention under any desired expressed conditions or within certain territorial limits or for limited periods. The law does not require that licenses be recorded. Such licenses may be either verbal or written. Unless the patentee is a reputable person, the purchaser of the title to the patent may find that previous licenses have substantially detracted from the value of the patent.

Period of the Monopoly. In the United States the patented monopoly is seventeen years [7] from the date of the issue of the patent, except that design patents are granted for a period of three and one-half years, or seven years, or fourteen years, as the applicant may elect. Many years ago the law provided that patent monopolies might be extended, but that provision of law has been repealed and now no patent can be extended except by act of Congress. If, however, improvements on the original are made, such improvements may be protected by patent and thus frequently the monopoly is, in effect, continued for a longer period than the seventeen-year original grant. The original patent may cover the disclosed invention only in a crude way; refinements come with practice, and such refinements may fairly be protected. In many cases the protection on improvements would exist without specific patents on such improvements, since the original invention during the seventeen years' monopoly may so improve the art that successful competition is not to be feared. Of course, such a condition does not apply in all cases.

Disclaimers and Reissues. An inventor may find, after his patent is granted, that he has claimed more than he originally invented or was entitled to. In such case he may prepare and file in the Patent Office a paper containing a disavowal or disclaimer of such excessive claims, retaining, however, that part of his invention which is truly his. The patent remains valid for the parts which are justly and truly his invention. Such a paper is called a disclaimer. The advantage of a disclaimer lies in the fact

[7] In England, 16 years; Canada, 18; Belgium, 20; France and Germany, 15 years. A revision of the French law makes the period 20 years after 1933. In Germany, the period is reckoned from the date of the filing of the application; in this country, it is reckoned from the date of issue, an important difference.

that the danger of invalidity is thus removed if the question becomes an issue in the courts.

A patent may be found to be invalid or inoperative because of inadvertence, oversight, accident, or mistake without fraudulent or deceptive intent; in that case, it may be surrendered to the Commissioner of Patents, who on proper showing will reissue it in the corrected form. The statute does not state how long a period may elapse after the issue of a patent before a reissue must be applied for, but many decisions have held that a lapse of more than two years is fatal to the grant of a valid reissue.[8]

Foreign Statutes. A United States patentee has the right to apply for patents in countries foreign to this country. He must claim these rights within twelve months from the date of filing his application in this country if he wishes to preserve his original filing date; or he may file his foreign patent applications at any time before the actual issue of his patent in this country. If he does neither of these things he loses the opportunity of securing a monopoly in many countries. So far as novelty is concerned, the laws of substantially all foreign countries provide restrictions similar to those existing in this country. Most foreign patents, however, are subject to taxes and in many foreign countries manufacturing of the inventions must be done within a year or more after the grant of the patent in those countries.[9] Unless the foreign taxes are paid and the foreign manufacturing requirements complied with, the patents in most foreign countries are thereby rendered invalid.

No taxes are payable on Canadian patents. In Great Britain taxes are payable only after the expiration of the fourth year of the life of the patent. There are more than one hundred and fifty different countries in which patent laws exist.[10] The question of whether a foreign patent should be taken out depends largely on the subject matter of the invention, and the industrial condition of the country in question.

It should be here noted that an invention patented in a foreign country, and not patented in the United States, may be legally made, used, and sold by any one in this country. Likewise, an invention patented only in the United States may be used by anyone in any country foreign to the United States without violating any legal rights of the patentee.

Infringement. Suits for infringement must be brought in the Federal District Courts by means of a bill of complaint. The defendant files an answer to the bill of complaint. Many defenses may be set up in the charge of infringement, such as anticipation by means of prior patents, prior pub-

[8] The importance of not leaving out an essential and integral step in the original patent from the reissue application is shown in a decision reported in *Chemical and Engineering News*, 20, 671 (1942).

[9] This is a serious handicap for the American patentee; the foreign patentee who has registered his patent in the U. S. Patent Office is not required to manufacture here.

[10] All countries do not have the same methods or rules for judging and issuing patents. French patents issue immediately and without examination, hence they serve as advance signals for patents filed in other countries, and their factual value is small. German and Dutch patents issue slowly and after painstaking examination, so that they are more apt to be limited to genuinely novel subject matter. The British patents and Canadian patents are about equivalent in stringency of judgment to the United States patents.

lications, or prior public use, or on the grounds of insufficient disclosure, absence of utility, inoperativeness, or aggregation. Of course, proof of non-infringement is sufficient to cause the bill of complaint to be dismissed.

Prior to the trial of a patent suit in the courts, depositions of fact witnesses may be taken, providing such witnesses live more than one hundred miles from the place of trial. These depositions are taken by either oral or written interrogatories upon examination and cross-examination of the parties to the suit or their attorneys. After being taken, such depositions are filed with the trial court and become a part of the trial record. Experts giving depositions relating to the subject matter of the patent involved must give their testimony in open court. The court rules provide that if the court understands the matter and does not desire such experts, such expert testimony is not permitted.

A suit brought for damages, profits, and for an injunction is an action in equity, and is tried before a judge without a jury; a suit to recover damages only, is tried before a judge and a jury.

In former years, probably in 90 per cent of the successful patent suits, claims for profits and damages were waived because of the difficulty of legally establishing them; within the past few years, however, court decisions have modified the rules as to the burden of proof so that it is much easier for the plaintiff to establish proof of profits and damages and much more difficult for the defendant to escape claims for such profits and damages. Recoveries in patent suits are, therefore, much more common now than formerly.

Shop Rights. If an employee in a manufacturing plant makes an invention while in such employ on the time and with the materials of his employer, and thereafter secures a patent on such invention, the company or individual owning the plant has what is known as a shop right or a shop license; that is, the employer can make, use, and sell the patented invention in such plant without the consent of the patentee. The monopoly of the patent, however, outside of the plant, is still solely vested in the patentee. Frequently the employee assigns his patent to his employer and relies on his employer's fairness for his reward. In some companies a contract between the employer and the employee is made, and provides that any invention made by the employee, during the term of his employment, which relates to the business of his employer, shall become the property of the employer. In such contracts, the title to the invention must be legally transferred to the employer. Shop rights, however, under the conditions named, even in the absence of a contract, remain with the employer.

Marking Patented Articles. If patented articles or the containers fail to bear the word "patented," or an abbreviation thereof, together with the date of issue of the patent, no damages or profits can be collected from infringers, unless proof be made that they have had actual notice of the patent. Usually the words "Patent applied for" or "Patent pending" are placed on articles of trade if patent applications have been made, but there is no provision of law requiring such marking, and such marking is regarded only as a warning.

Patent Publications and Services. Annually the Patent Office issues an indexed volume giving the names of all patentees of that year, and a list of the subjects upon which patents have been taken out.

Besides the collection of the full-text patent specifications, there is issued by the various patent offices a journal containing abstracts of the full patents. The United States Patent Office publishes the "Official Gazette of the U. S. Patent Office," in which the abstracts are arranged numerically. For the Canadian specifications, there is published the "Canadian Patent Office Record." The Patent Office in London publishes the "Illustrated Abridgements of Specifications"; since January 1st, 1931, the British Abridgements are classified in 40 groups. A list of these groups with their content in terms of previous classifications of 146 groups, will be found in the Index volumes of the Abridgements, or may be sent for directly. The three publications just mentioned will be found in many of the public libraries in the United States, deposited there free of charge by the several Offices for the convenience of the public. Such libraries will usually have a complete file of the United States full-text patent specifications, also a gift from the Patent Office to the public. Full files of the patents specifications of all countries will be found at the Patent Office in Washington, and may be consulted by any one; given the number, the patent can be found, since they are arranged numerically. On request and payment of a modest fee, a photostat will be sent.

There is one more service offered which is of the greatest convenience. The Superintendent of Documents, Washington, D. C., will send for $1 the "U. S. Manual of Classification of Patents." After studying it, a request may be addressed to the Commissioner of Patents that all patents in a certain class, or subclass, be sent on, as fast as issued, without further notice; for this service, a fee of $1 per year per class is charged, plus the usual 25 cents for each copy. In this way, the subscriber receives at his desk every patent which pertains to his specialty without any labor on his part.

It will be well to note that the British Patents now have running numbers, beginning with January 1, 1916. Before that time, every year started with number 1, so that for British Patents it was necessary to give the year, as well as the patent number; this is no longer necessary for the patents issued since that date.

Beginning with January 1st, 1928, and with volume 22, *Chemical Abstracts*, published by the American Chemical Society, lists patents under the name of the assignee, in addition to the customary listings under the name of the patentee and in the Subject Index. This is a tremendous advantage for the reader, who often knows which firm is developing a certain patent, without knowing the name of the patentee.

Starting with January 1st, 1935, there is provided as Part IV of the index of *Chemical Abstracts* the numbers of the patents, for which abstracts have appeared, arranged in the order of the numbers, and grouped by countries. Knowing the number of the patent, the reader can find its abstract in a moment.

British patents will be found abstracted in *Chemical Abstracts* or in the abstracts of the *Journal of the Chemical Society* (London). A classified

collection of German medicinal and dye patents is the *Friedlaender*,[11] while patents dealing with the inorganic chemical industry are classified and reviewed in the Braeuer and d'Ans collection.[12]

Copyrights and Trade-Marks. Copyrights are granted under separate Congressional statutes for books, maps, periodicals, drawings, pictures, musical compositions, dramatic works, and the like. Such applications are not made at the Patent Office, but to the Registrar of Copyrights at the Library of Congress, Washington, D. C.

Trade-marks are registered in the Patent Office under the trade-mark laws; labels and prints are registered in the Patent Office under the copyright laws. The Registrar of Copyrights has sole jurisdiction of the registration of everything referred to in the copyright laws, except labels and prints. A label is defined as something applied to the goods or to the container; a print is not so applied, but serves separately as advertising. Both labels and prints must be distinctive in appearance, and must be the result of original creation.

Reading References

"The law of patents for chemists," Joseph Rossman, Washington, Inventors Publishing Co., 1932.

"Principles of patent law for the chemical and metallurgical industries," A. W. Deller, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1931.

"Patent rights for scientific discoveries," C. J. Hamson, Indianapolis, Bobbs-Merrill Co.

"Principles of patent law involved in the Weiss patent litigation (over di-phenylguanidine as an accelerator for rubber vulcanization)," A. W. Deller, *Ind. Eng. Chem.*, 20, 1361 (1928).

Some important patent decisions are listed in *Ind. Eng. Chem.*, 23, 7 (1931).

"Patents," A. H. Walker, New York, Baker, Voorhis & Co., 5th ed., 1917.

"The law of patents," W. F. Rogers, Indianapolis, Bobbs-Merrill Co., 1914.

"Copyright law," A. W. Weil, Chicago, Callaghan & Co., 1917.

"The law of chemical patents," E. Thomas, New York, D. Van Nostrand Co., 1927.

"An outline of the law of chemical patents," E. Thomas, *Ind. Eng. Chem.*, 19, 176, 315 (1927).

"Patent law for chemists, engineers and executives," F. H. Rhodes, New York, McGraw-Hill Book Co., 1931.

The German patent law and regulations are stated in the *Chemiker-Kalender for 1932*, Vol. III, p. 574-592, Verlag Julius Springer, Berlin; with a table of sundry patent information covering 23 countries.

"The preparation and prosecution of patent applications," Charles W. Rivise, Charlottesville, Va., The Michie Company, 1933.

"Legal pitfalls for the chemical engineers," J. Davidson Pratt and G. S. W. Marlow, *J. Soc. Chem. Ind.*, 53, 235 and 261 (1934).

"Patent law and practice of foreign countries—Foods and Drugs," Thomas H. West, *Ind. Eng. Chem.*, 30, 1424 (1938).

"Needs of our patent system," Delos G. Haynes, *Ind. Eng. Chem.*, 30, 1430 (1938).

"Technical report writing," Fred H. Rhodes, New York, McGraw-Hill Book Co., 1941.

"Inventions and their management," Alf K. Berle and L. Sprague de Camp, Scranton, Pa., International Textbook Company, 1941.

"More on Patents," *Ind. Eng. Chem.*, 32, 598 (1940).

"Rules of practice in the United States Patent Office," published by the Patent Office, U. S. Department of Commerce; revised October 1, 1940.

[11] See reading references for Chapter 28.

[12] *Fortschritte der anorganisch-chemischen Industrie*, by Adolf Braeuer and J. d'Ans, in several volumes, published by J. Springer, Berlin.

An industrial chemist must be acquainted with the appliances suitable for large-scale operations, as distinct from laboratory practice; the proper choice of the specific appliances depends upon such acquaintance. It would be too much to say that the success of a process depends upon the proper choice of auxiliary devices, but its difficulties will certainly be greatly lessened.

Chapter 41*

Appliances Used by the Chemical Engineer
I. Pumps, Fans, Blowers, and Compressors

Pumps are used to move liquids from one point to another, frequently to an elevated point. The simplest pump is the trench pump, which has a short barrel, a piston moved up and down by a hand lever, and, mounted in the piston, a clap valve opening on the down stroke and closing on the up stroke. As the piston is lowered, a gallon or so of water passes through the valve to the barrel above the piston; on the up stroke this amount of water is pushed up and discharged through a lip to a runway.

For industrial purposes, pumps are operated by steam or electric motors, or they may be belt-driven or gear-driven; the latter are known as "power pumps." The variety in principle and design is considerable. A classification might be made as follows:

1. **Reciprocating pumps,** in which the pumping element has a back-and-forth motion, may be further divided into piston pumps, plunger pumps, and diaphragm pumps. The piston pumps are double-acting, that is, each side alternately pushes or sucks; if there is one piston, it is simplex; if there are two pistons, working on the same suction and discharge line, it is duplex; if there are three, it is triplex. The discharge from the duplex pump is more even than that from the simplex. The valves are located in an enlarged portion of the suction and discharge lines.

The plunger pump has a closed, hollow cylinder as the pumping element. In the vertical type it is single-acting, but usually triplex; in the horizontal type two plungers may be placed, working opposite each other. The piston pump is usually steam-driven, with the steam piston on the main pump shaft; the vertical triplex plunger pump is usually a power pump.

2. **Rotary pumps** with direct action are those which push the liquid bodily; examples are the gear pump, the sliding vane pump, and the two-vane pump such as the Roots-Connersville. The rotary pumps with indirect action, impelling rather than pushing, hence imparting a velocity, are the centrifugal pumps; the impeller may be "open," or if the vanes are cast between two disks, "closed." A centrifugal pump may work singly, the usual practice in chemical plants, or in stages; each stage has its own impeller and casing.

* Chapters 41 to 44, and 46, have been expanded and published in book form, under the title "Chemical Machinery," by Emil R. Riegel, New York, Reinhold Publishing Corporation, 1944, with a second printing 1947 (corrected).

3. The acid egg, often called a blow case, is also a pump in the sense that it serves to move liquids, and slurries, from one place to another; the driving force is compressed air, and its operation may be automatic.

A ram is a special type of pump in which the feed water itself supplies the driving force.

Reciprocating Pumps. This structure and operation of the **piston pump** are illustrated in Figure 272. On the stroke from left to right, the water is pushed by the front end of the piston, valves *LP* are depressed, and delivery is made to the pressure line; valves *RS* are held shut by the pressure, so that the suction line is closed. In the meantime and on the same stroke, the crank end of the piston has drawn in water through *LS*, but

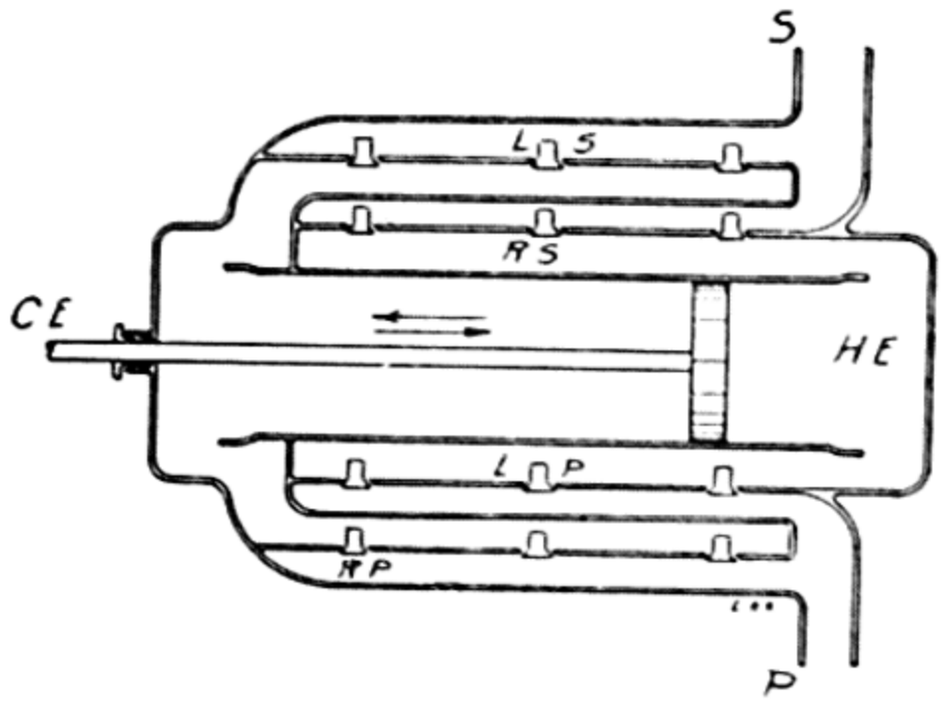


FIGURE 272.—Sketch of a double-acting piston pump. *CE*, crank end; *HE*, head end; *S*, suction line; *P*, pressure or delivery line. *See* text.

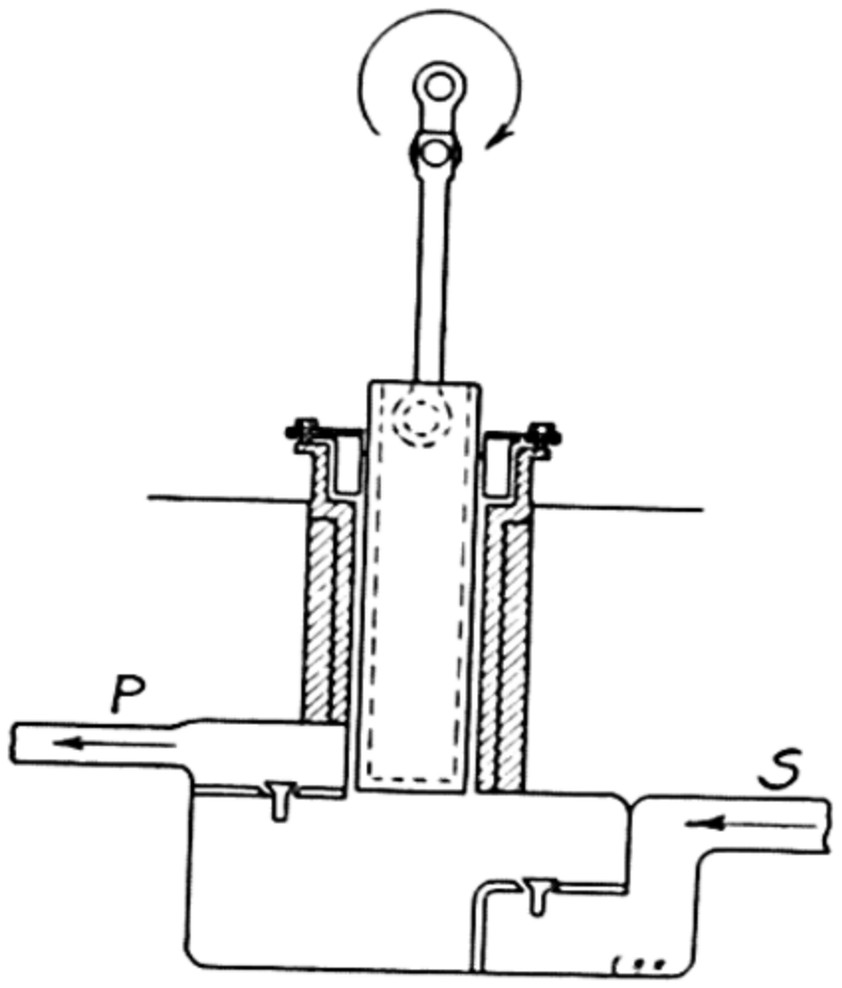


FIGURE 273.—A plunger pump; *S*, suction line; *P*, pressure or delivery line.

held *RP* closed. On the return stroke, right to left, the crank end of the piston exerts pressure, forcing the valves *RP* open, and delivering the water to the pressure line; the head end of the piston on the same trip draws in water through *RS*, while *LP* stay closed. Such a pump would be double-acting.

The valve may be circular and may carry a rubber ring working on a metal seat; or ball valves may be preferred, consisting of a metal ball working against a metal seat, and fitted with shoulders which prevent their unseating more than just enough to let the water through. Ball valves require no spring; they seat by their own weight; but flat valves are held shut by a steel spring, which is chosen so thin that it exerts just enough pressure to seat; the pressure is so weak that very little pressure by the water causes it to unseat. The stem of the valve acts as a guide, causing it to seat properly. In the sketch of the piston pump, the springs holding the valves shut are not shown.

A plunger pump is shown in the adjoined sketch. The plunger is a cylindrical boot, with only one working side; hence it is single-acting. As

shown in Figure 273, the plunger is at the end of the down stroke, and ready to rise. The play of the valves will be clear from their positions.

The piston pump has its packing in the piston itself, while in the plunger pump the packing is in a stationary stuffing box forming part of the casing.

In the boiler house, either piston or plunger pump is used to feed water into the boilers (feed pump); high-speed centrifugal pumps are now also used for that purpose. For forcing a muddy liquid through a filter-press, pressures of 40 to 60 pounds are often required and a triplex plunger pump is well adapted. The speed varies greatly with the kind of service performed, but in general, it is rather low, 30 to 60 double strokes per minute.

In the **diaphragm pump** the liquid to be moved does not come in contact with the pumping element. An example of this type of pump is the Dorrco.

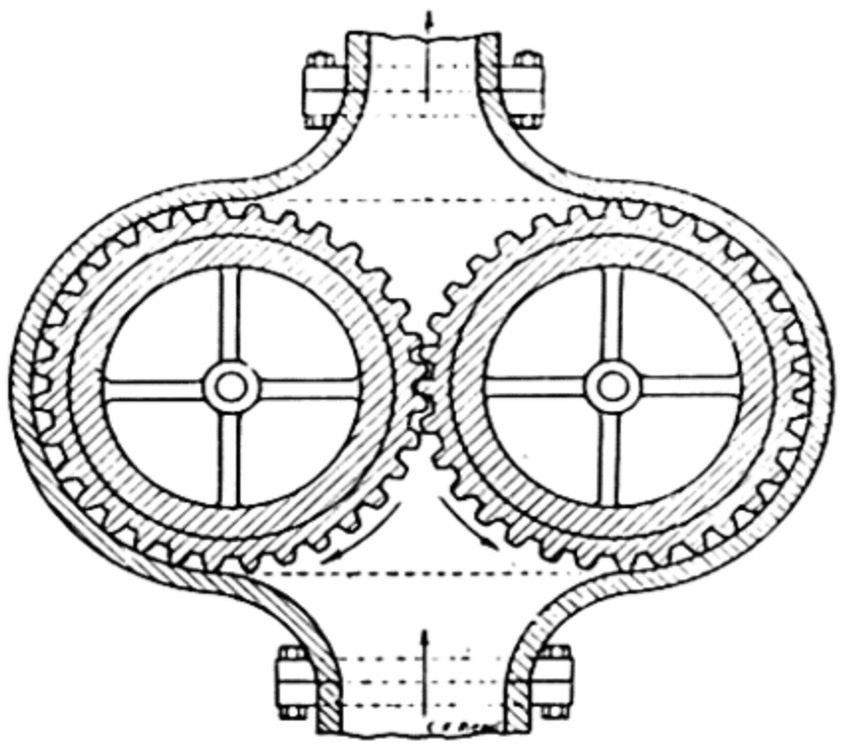


FIGURE 274.—A gear pump.

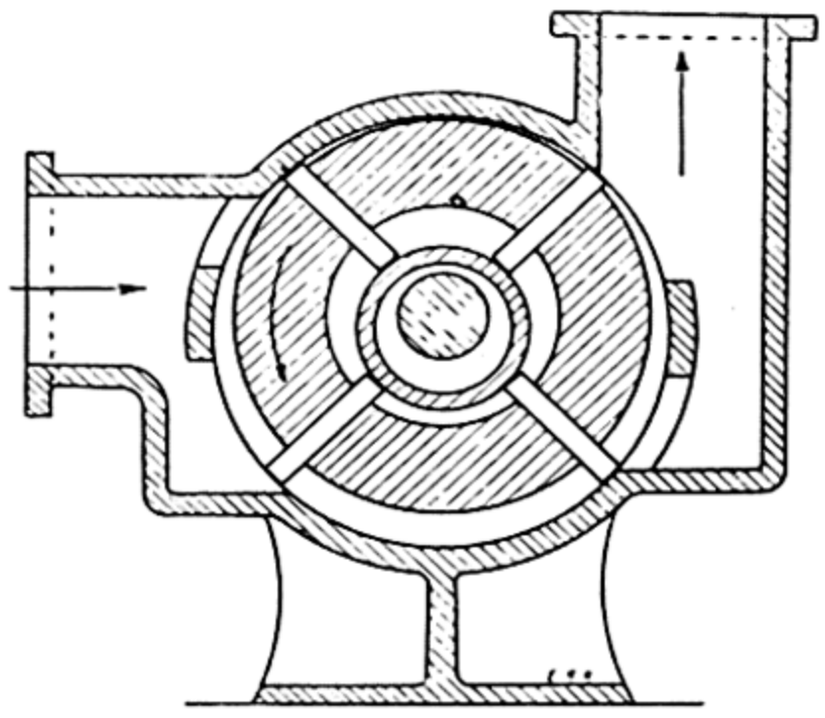


FIGURE 275.—A sliding vane pump, of the ring type.

Rotary Pumps with Direct Action. The gear pump, shown in Figure 274, carries the liquid between the casing and the teeth of the gears. The friction is considerable, and the gear pump is therefore chiefly used for oil and other liquids which have lubricating properties. The size is nearly always small, and the capacity of the pump correspondingly small; its simplicity and reliability have led to its general use for such purposes as pumping fuel oil to the burner.

In the **sliding vane pump,** (Fig. 275) the rotor and shaft are eccentric to the casing; the rotor carries each slide in and out because they rest on a stationary ring which is centered; the casing itself is circular. This type of sliding vane pump is the ring type [1]; its operation will be clear from the sketch. There are many other modifications of this pump; in the earlier models, the casing was elliptical. The sliding vane pump has again no valve in the strict sense; it has wide passages, so that it is well adapted for slurries, and for liquids carrying lumps of soft solids. The sizes are rather small; the suction line varies from 1 to 4 inches, although larger sizes may be built and operated with fair efficiency. The pump with 4-inch suction line and 4-inch discharge line has a capacity of 200 gallons per minute at a speed of 150 r.p.m.

In the **two-vane pump,** the action is the same as in the gear pump; the water is pushed between the casing and the vane; the operation is indicated

[1] Such as manufactured for example by the Taber Pump Co., of Buffalo, N. Y.

in the four-stage figure adjoined (Fig. 276). Each vane shaft carries a toothed wheel, and the two wheels mesh; one shaft carries the driving pulley, which causes both to rotate against each other. Such pumps are made in small as well as very large sizes; a capacity of 63 cubic feet per revolution is still below the maximum. The speed is moderate (up to 250 r.p.m.).

Centrifugal Pumps. A centrifugal pump is a rotary pump with indirect action. The moving element is a disk, usually vertical, rotated by a hori-

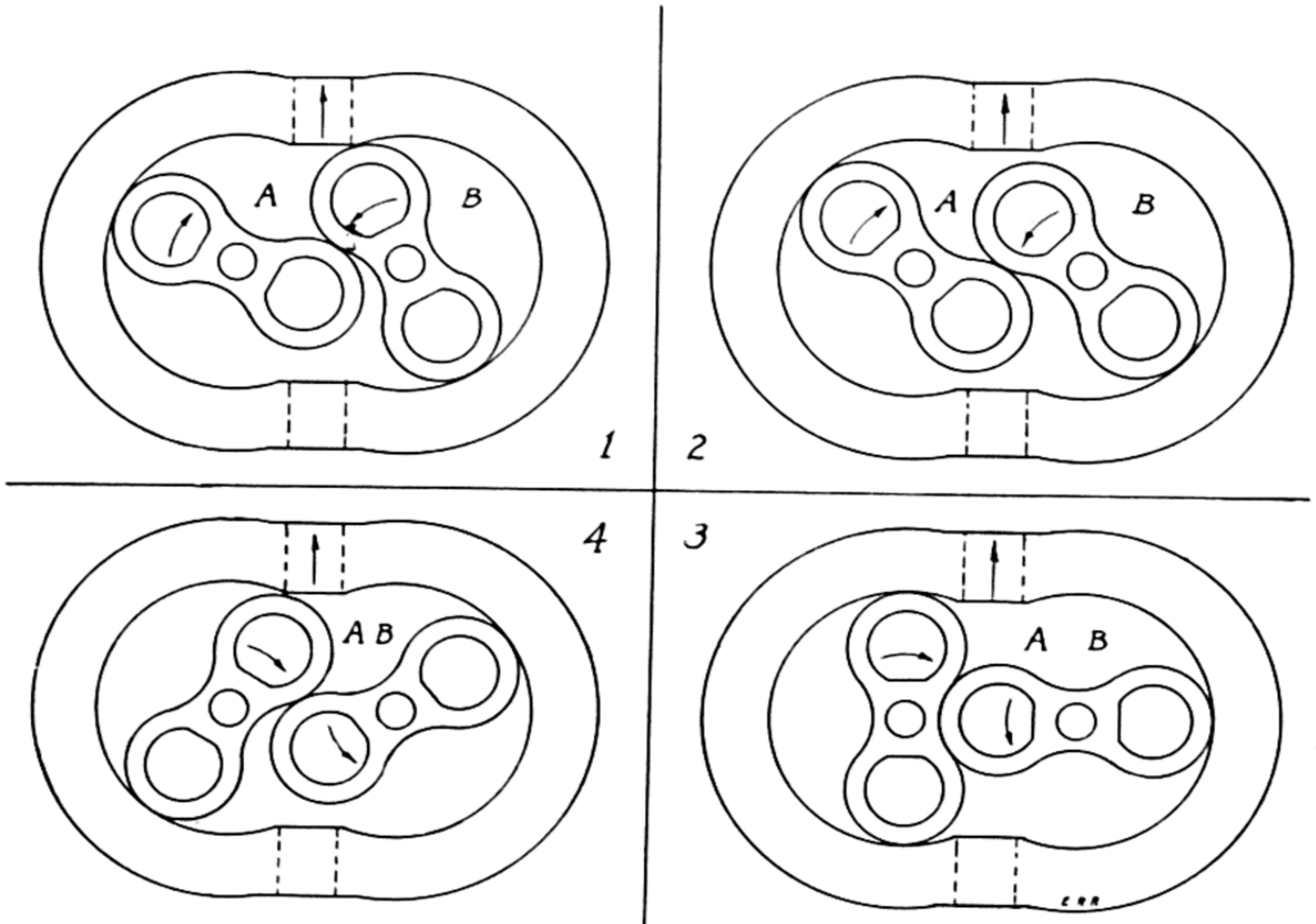


FIGURE 276.—Four stages in one-third of a revolution in a Connersville blower, of the two-impeller type; Stage 1, volume *B* is ready to be discharged; Stage 2, *A* and *B* are a maximum, *B* is beginning to pass to delivery outlet; Stage 3, *A* and *B* smaller than in 2; Stage 4, *A* and *B* a minimum; the difference between *AB* in Stages 1 and 4 has been discharged.

zontal shaft; the disk carries curved blades, and is contained in a spiral casing with close-fitting side walls. The water enters through an opening facing the center of the disk, and the water is caught in the channels between the blades; the latter do not quite reach the central part of the disk. The water is delivered to the gradually widening spiral part of the casing; it receives a high velocity from the rapidly rotating wheel, and passes out of the casing to the discharge line with essentially the same velocity. Figure 277 is a sketch of a simple, open-impeller type centrifugal pump, single-stage. In the two- and more-stage pump, the discharge of the first stage becomes the feed of the second.

Low-pressure, single-stage centrifugal pumps are employed with satisfactory efficiency, equal to that of piston pumps, for lifts of 30 to 50 feet (water); the efficiency usually given is 50 to 60 per cent. For lower lifts,

the efficiency is higher; for lifts of 90 or 100 feet, the consumption of power becomes enormous and the efficiency correspondingly low. The speed of the centrifugal pump is comparatively high; 1200 r.p.m. is a frequent speed, and 1800 not uncommon. The impeller shaft is direct-connected to an electric motor shaft, or belt-driven. The direct-connected pump with its motor forms

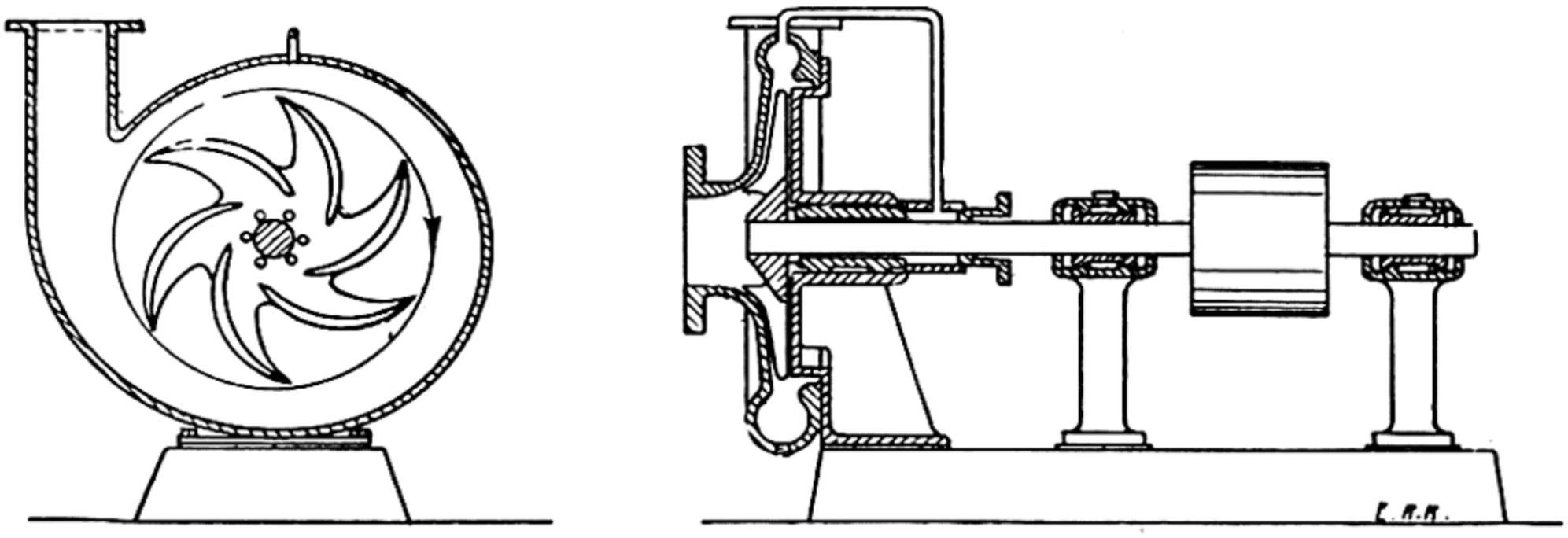


FIGURE 277.—A centrifugal pump, single-stage, open-impeller type.

a compact pumping unit which has come into high favor; it occupies very little floor space, and operates so noiselessly that from a short distance it is impossible to tell whether it is in operation or not. All remarks in this paragraph apply to a single-stage pump; the multiple-stage pump produces higher heads with satisfactory efficiency. For viscous liquids, the centrifugal pump is useless. In giving the heads on the discharge side of the pump, it is assumed that the water floods the pump. If the water enters under a head of 15 feet the pump will raise the discharge water that much higher.

The LaBour pump shown in Figure 278 is the most recent member of a long line of pumps which have served the chemical industries; it is a self-priming centrifugal pump, with vertical impeller.

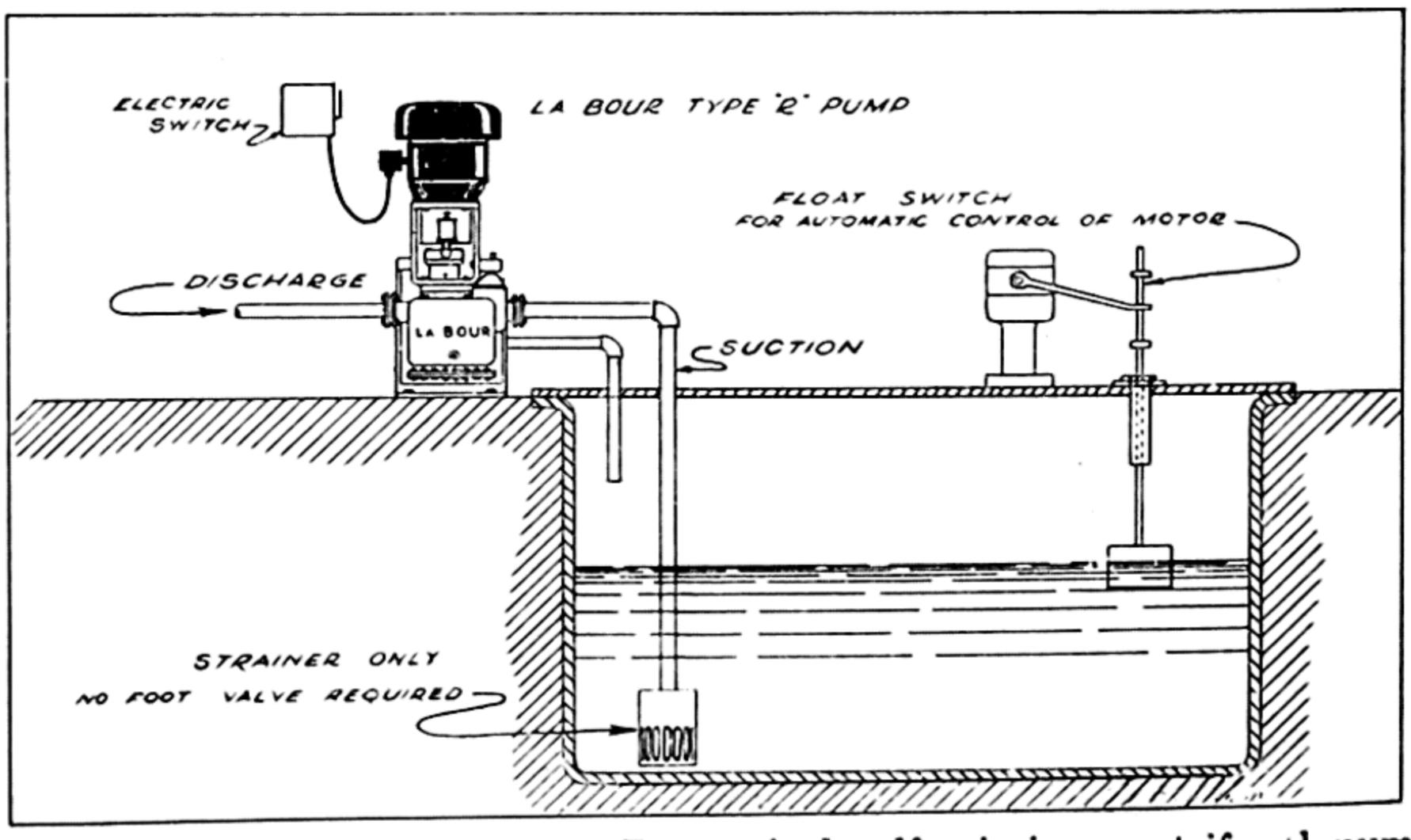


FIGURE 278.—The LaBour, type R, vertical self-priming centrifugal pump applied to sump service. The pump may be controlled by automatic float switch. No foot valve is required in the suction line. (The LaBour Pump Company, Inc., Elkhart, Indiana.)

If the water to be pumped must be drawn up from a lower elevation, the centrifugal pump must be primed, that is filled with water, and the whole suction line also, before it can pump. The suction lift must not be over 28 feet, for any type of pump, piston pump included. It may be noted also that the centrifugal pump has no valve, hence is adapted to muddy liquids.

Next in complexity to the open impeller is the closed impeller, usually of bronze, consisting of two disks separated by the curved blades which act on the water; the casing is close-fitting on both sides of the double disk. The variety in construction is very great. In size centrifugal pumps are built with 20-inch suction line and smaller; in industrial plants, the 3- and 4-inch suction line is the general practice.

For certain purposes, such as fire pumps and boiler-feed pumps, centrifugal pumps are used which are driven at speeds varying between 3000 and 20,000 r.p.m. and even more; for such speeds, it is general to use the steam turbine as the driving mechanism.

The centrifugal pump may be considered a water turbine reversed; instead of a flow of water driving the shaft of the generator, it is the generator shaft which rotates the water wheel and drives the water in the opposite direction (Chapter 12).

Fans, Blowers, Exhausters, and Compressors

For the propulsion of air and gases, fans, blowers, and exhausters are employed. A fan moves a great volume of air (or gas) at slight pressure; for instance it may take the exhaust gases from a blast furnace and deliver them to the base of a tall stack. The word "fan" covers both blowers and exhausters: a blower takes fresh air from the outside and delivers it to a desired point; an exhauster takes foul air from a certain room and delivers it to the outside air. The essential operation of the blower and exhauster is the same, but the openings in the casings differ.

Fans are volume blowers; compressors are pressure blowers. The compressor delivers a small quantity of air at a high pressure; between the two extremes there are machines which deliver considerable volumes at appreciable pressures, for example 3550 cubic feet per minute at the pressure of 24 inches of water. Such devices are often called pressure blowers, but they may be classified as low-pressure compressors. A fan of medium size would be one which delivers 11,400 cubic feet of gas per minute against a pressure of one-fourth inch of water.

A fan may have 6 or 8 flat steel blades, or in a different type, 60 very small curved blades; the latter would belong to the multi-bladed type.

Compressors furnish air or gas at a high pressure, compared to the pressure against which a fan works. The low-pressure compressor described above works against a pressure of less than one pound; it is a single-stage machine, and such single-stage compressors are suitable for pressures up to 50 pounds. For pressures between 50 and 500 pounds, double-stage compressors are used, with an intermediate cooler. For pressures between 500 and 1000 pounds, 3-stage compressors, and for pressures above 1000 pounds, 4-stage compressors are used, with cooling between stages. A single-stage

compression to a very high pressure is not practical [2]; the heat developed is so great that on cooling in the conduits, a much lower pressure would be obtained. The heat on compressing must therefore be removed, and the cold compressed gas, at 50 pounds for example, may then be compressed a second time.

Fans are generally belt-driven, usually from a special motor. Low-pressure compressors are also belt-driven; high-pressure compressors are direct-connected to steam pistons, or to motors.

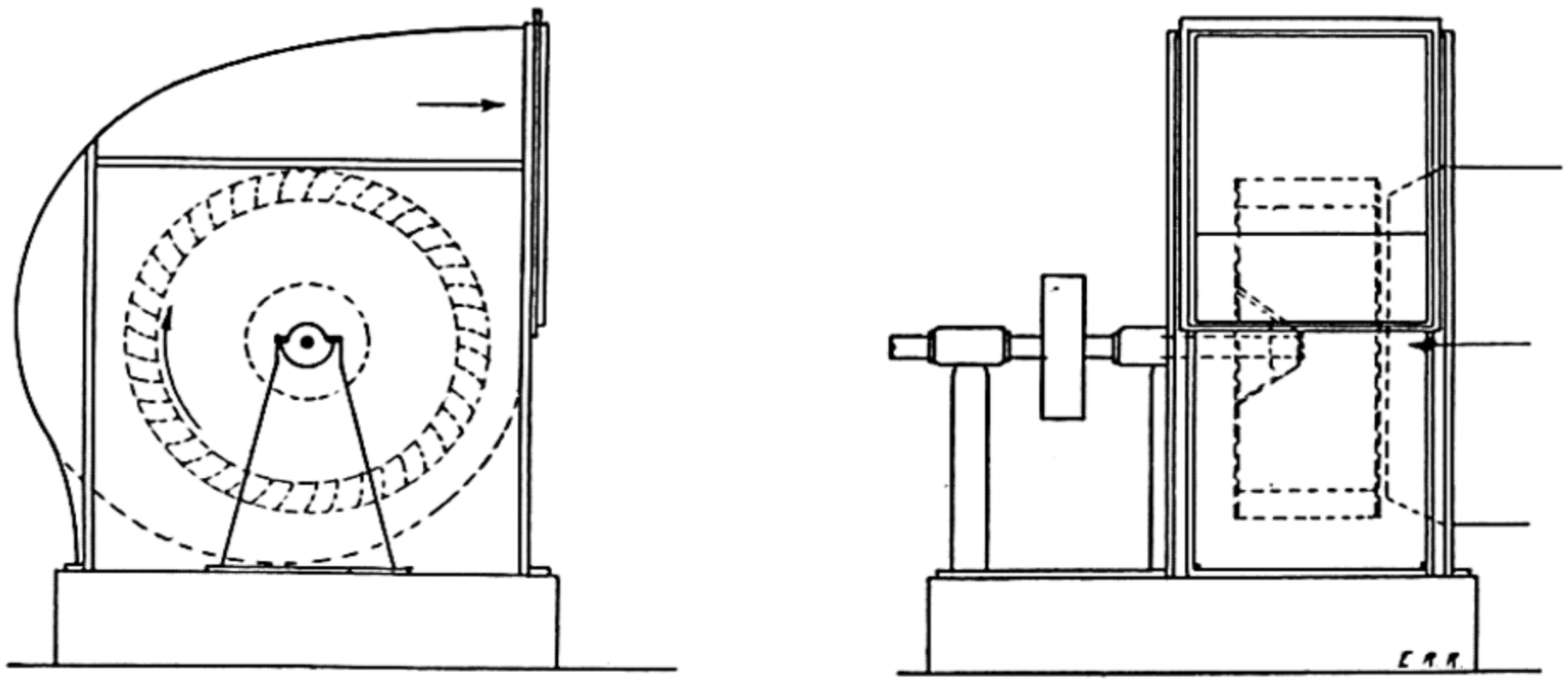


FIGURE 279.—A multi-bladed fan.

Multi-bladed Fans. A multi-bladed fan, the Sirocco,[3] is shown in Figure 279. The volume of air moved by the fan depends upon the speed of the wheel and upon the pressure. The higher the pressure against which the fan discharges, the lower the volume discharged; the lower the speed of the wheel, the lower the discharge. Furthermore, the lower the pressure of the air entering the fan, the lower the volume discharged.

The capacity of any fan or compressor is computed on the basis of free air, that is, air at atmospheric pressure and at 60° F. (15° C.); if the gas moved is at an elevated temperature, the volume moved, computed to its true volume at 60° F., will be less than if it had been cold. All these factors are taken into consideration in the tables of capacities which the manufacturers supply on request.

Compressors. A low-pressure compressor used extensively in the chemical industries is the Connersville blower, of the same construction as the two-vane pump described in the first part of the chapter. The Connersville blower gives pressures varying from a fraction of a pound to eight pounds per square inch. It is manufactured in all sizes. A medium size would be the 13-foot capacity compressor, which, run at 350 r.p.m., furnishes 4550 cubic feet (calculated) per minute, actually 3640 cubic feet; the difference is due to a slip between the casing and the vane and between the two vanes.

The Nash Hytor is also a low-pressure compressor, furnishing air under pressures of the same range as the Connersville. Its contruction and opera-

[2] The compression curve is too near the adiabatic curve and too far from the isothermal curve.

[3] Made by the American Blower Company, of Detroit, Mich.

tion will be clear from Figure 280. The elliptical casing contains water which alternately leaves the rotor, and fills it. The air is carried in the buckets formed by the vanes and the liquid, from the inlet *A* to the outlet *B*. The small sizes for 50 cubic feet of free air per minute (against 10-pound pressure) have a speed of 1600 r.p.m.; the large size, for 2250 cubic feet discharge against the same pressure, has a speed of 230 r.p.m. The Nash Hytor may be built of special metal, and is used with concentrated sulfuric acid as working fluid for the compression of chlorine gas (Chapter 5).

High-pressure compressors resemble piston pumps, except that the valves are feather valves as a rule. The feather valve (Laidlaw) is a thin, flat steel plate, held against the shoulders of a port by a suitable frame. It

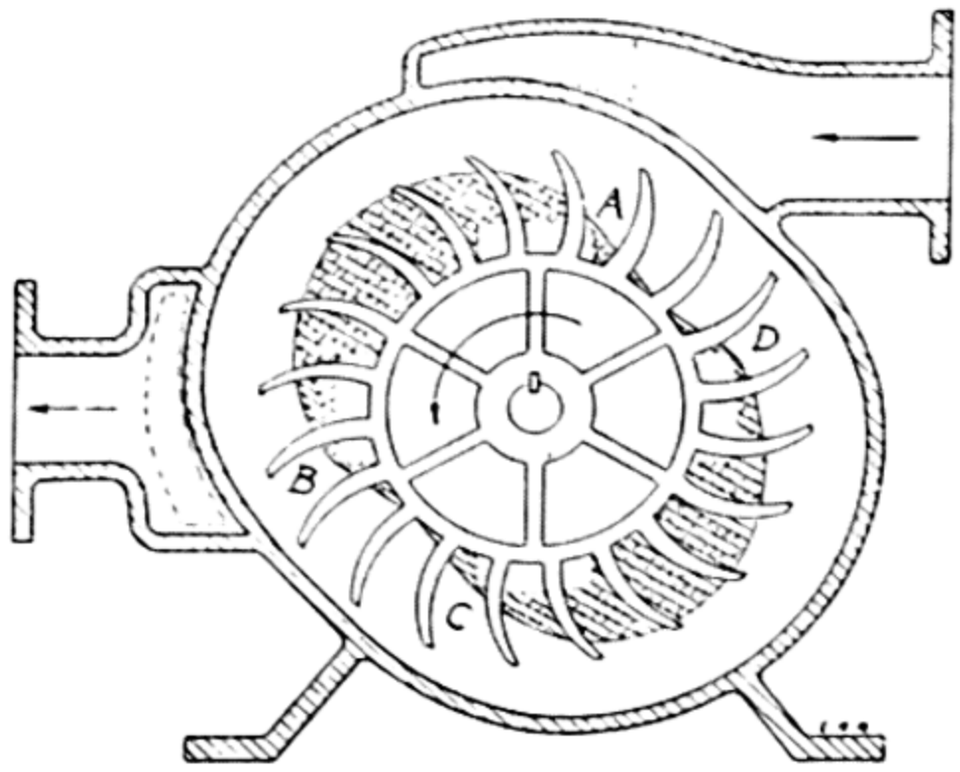


FIGURE 280.—The Nash Hytor (compressor). *A* and *C* are inlet ports, *B* and *D* outlet ports. The cross-hatched areas represent the gas volume being moved, the clear area within the casing, the liquid employed.

can lift from the seat one-thirty-second of an inch, or similar distances, which are sufficient to allow the compressed air to pass to the other side of the valve. Cooling between stages is by means of tubes laid in cold water. The development of the direct synthesis of ammonia from atmospheric nitrogen and hydrogen has greatly stimulated the design of high-pressure compression.

VALVES AND PULLEYS

For water lines and for liquids in general, the slot or gate valve is used, especially if the liquid is not under pressure. For steam lines the globe valve is employed; it has a pressure side and a discharge side, and is so placed that the pressure of the steam (also water) is exerted on the under side of the movable disk. In addition to these two, the chemical engineer has utilized the plug valve, operated from a threaded stem above, or from levers with joint below the bottom of a tank. The plug valve has the advantage that, when it is opened, the passages for the liquor or slurry are wide and not easily obstructed. Plug valves are frequently home-made. Besides valves, cocks are used in water and steam lines.

A pump may be driven by a belt which receives its motion from the pulley of a motor; in that case the motor pulley is the driving pulley; the pump pulley, the driven. The number of revolutions per minute of the two pulleys is inversely proportional to their diameters or their circumferences. For pumps driven by gears the relation of the revolutions per minute is inversely proportional to the relation of the number of teeth on the pinion (small wheel) and gear (large wheel).

Other Patents

1,849,557, high pressure centrifugal pump of low capacity and economical operation; 1,849,127, a centrifugal pump, especially adapted for pumping more or less viscous materials or fluids such as sewage sludge; 1,863,160, rotary pump consisting of two intermeshing gears; 1,887,873, centrifugal fan, of the propeller type; 1,884,067, a fan for pneumatic blowers; 1,821,484, spiral blade fan, designed especially for use in connection with air-cooled engines; 1,778,041, vertical blower of the propeller type, with a convergent-divergent casing; 1,787,062, multiblade blower; 1,853,973, centrifugal compressor or blower; 1,854,692, compressor and vacuum pump for air and other gases, which has a rotary member which is eccentrically mounted within a cylinder and provided with blades movably mounted in slots and which engage the inner face of the cylinder, thereby forming pockets within which the air is gradually compressed as the rotor turns, due to the progressively decreasing volume of the space between it and the wall of the cylinder; 1,816,403, high-pressure reciprocating piston compressor; 1,867,651, hydroair compressor and vacuum pump (rotary pump having a series of buckets).

Reading References

"Fan engineering," W. H. Carrier, 2d ed. revised by R. D. Madison, published by the Buffalo Forge Co., Buffalo, N. Y., 1925.

"Hypercompressor," R. W. Miller, *Chem. Met. Eng.*, 37, 571 (1930).

"Pumps," Chas. W. Cuno, *Ind. Eng. Chem.*, 24, 1109 (1932).

"Mechanical engineers' handbook," L. S. Marks, New York, McGraw-Hill Book Co., 1942, Section 13.

"Elements of hydraulics," M. Merriman, New York, John Wiley and Sons, Inc., 1912.

"The electrical engineers' handbook," International Correspondence Schools, Scranton, Pa.

"Pumps" (types, selection, installation, operation, and maintenance), Frank A. Kristal and F. A. Annett, New York and London, McGraw-Hill Book Co., 1940.

"Selection of pumps for chemical service," Ward E. Pratt, *Ind. Eng. Chem.*, 31, 408 (1939).

"Centrifugal pumps for the process industries," H. E. LaBour, *Ind. Eng. Chem.*, 30, 1105 (1938).

"Power pumping," F. A. Annett, *Power*, p. 315-330, June, 1938.

"Chemical Engineers' Handbook," John H. Perry, New York, McGraw-Hill Book Co., 1934.

The task of separating a solid from the liquid in which it is suspended presents itself in nearly every chemical plant; this task can be discharged successfully only if the plant chemist is acquainted with all types of devices suitable for such separations.

Chapter 42

Appliances Used by the Chemical Engineer
II. Filters

The separation of comparatively small amounts of solids from larger amounts of liquids is done by settling, followed by decantation of the supernatant clear liquid, or by the use of a filtering device. The separation of very small amounts of liquids from large amounts of solids is done by draining, or by centrifuging.

Settling out the solid is the cheapest method, and is frequently used. If the operation is extensive, a large capacity in settling tanks is required; these act also as storage tanks. If the liquor is hot, the tank may be insulated by strips of wood. As a rule, this process is too slow; also, the mud collected in the bottom of the tank still contains too much water, and is usually sent through a filter, a combination of settling and filtering.

Filtering devices include gravity filters, pressure filters, more commonly called filter-presses, and suction filters. Several points must be considered when studying a filtration problem: whether the cake or the filtrate is the valuable part, whether or not washing is required, and whether the operation should be continuous or intermittent. These considerations will have weight in the choice of the device. Other considerations are capacity, first cost, and operating cost, which includes repair costs and, more important, operating labor. At the end of the chapter, these points will be reviewed.

The suspension to be filtered is called a slurry, if its content in solids is not so high that it does not flow and cannot be pumped; slurries contain from less than 1 per cent to 40 per cent of solids, by weight. Suspensions containing more than 40 per cent of solids are more properly called sludges. The solid separated in the filter device is called the cake, the clear liquor running off is the filtrate. Filtering devices such as filter-presses and suction filters are really frames for the support of the filtering medium, the filter cloth, which may be cotton duck of various thicknesses, muslin, paper, wool flannel, or metal wire woven into cloth, such as iron wire, nickel wire, and Monel wire.

The Gravity Filter. In the gravity filter, the slurry lies over a bed of sand over pebbles, for instance, with channels between the larger pebbles for the escape of the clear liquor. The mud is deposited on the sand; the liquor passes through by the action of gravity. The most extensive use of this type of filter is made in the filtration of drinking water on a large scale (Chapter 13).

A filter paper in a glass or porcelain funnel is a gravity filter; it is used in the fine chemical industry for manufacturing reagents and certain rare chemicals.

The Pressure Filters, Plate-and-Frame Type. The most familiar filter press is the plate-and-frame press; it consists of separate cast-iron square pieces, the plates proper, and the frames, which rest on two horizontal bars, and which may be squeezed together by a movable end-piece working against a fixed front end. The surfaces which touch are machined, so that the fit is perfect. Each frame is covered by a filter cloth which extends over all of it, and on both sides; when the press is closed, the edges of the cloth form the gaskets between the machined surfaces. The cloths are provided with small openings to correspond to the eyes in each plate and frame; in the closed press these eyes form a conduit on one side for the slurry, and on the other side, for the entering wash water. In Figure 281 three pieces are shown: a non-washable plate, a frame, and a washable plate. The openings

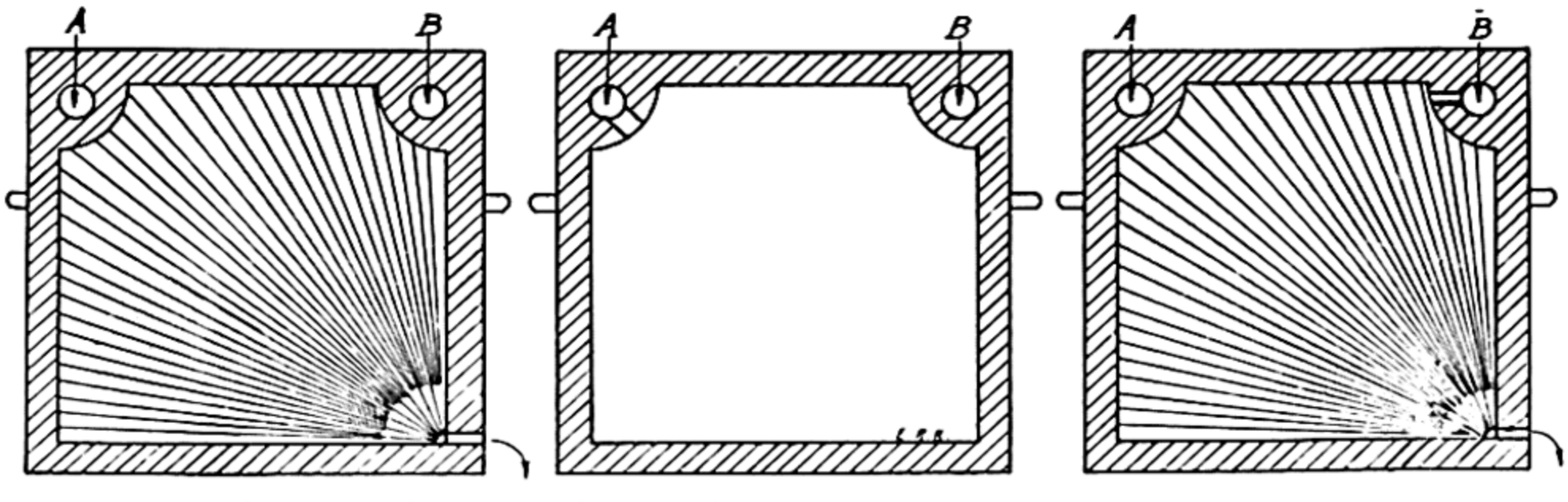


FIGURE 281.—Plates and frame for a filter press; to the left, a non-washable plate; in the center, a frame; to the right, a washable plate; the eyes at *A* form the slurry line, open only to the frame; the eyes at *B* form the wash-water line open only to the washable plate.

marked *A* form the slurry line; the only port in this line is to the frame. The openings marked *B* form the wash-water inlet line; its only port is to the washable plate, on the right. The non-washable plate has no ports. When filtering, both kinds of plates deliver the clear liquor at the outlet; the slurry enters in the frame, and its liquor passes through the filter cloth in order to reach the channels in the plates. As a rule washing must be done; if the liquid is the valuable part, none must be left in the cake; if the solid is the valuable part, the adhering liquid carries impurities which must be removed. When washing, the outlet of the washable plate, at the right, is closed; the one in the non-washable plate remains open. The wash must now pass through a cloth, through the cake, and through another cloth before it can reach the channels in the non-washable plate and from these, the outlet. The arrangements for filtering and for washing are shown in the two front views of five plates and five frames each.

Slurry is fed to the press until the frame is completely filled with cake; at this point, the pressure in the slurry line increases beyond the usual figure and at the same time, the amount of filtrate decreases. The washing will be imperfectly done unless every frame is filled with cake. As the first liquor passes through the cloth, it is turbid, and is run to an intermediate receptacle from which it is sent to the filter again; the reason for this turbidity is that the filtering is done not by the cloths themselves, but by a thin layer of mud which coats them in the first few moments. After a few minutes, the

filtrate is clear. If the solids are low, it may take 12 hours to fill the frames with mud; two hours is nearer the average time; the difference is due to the percentage of solids in the slurry, and to the size of the frames. When these are filled, the liquor line is closed, and the wash water is admitted through its conduit; the washing may be followed by testing the density of the liquid with a hydrometer; it is continued as far as the conditions warrant. If the cake is insoluble, and the wash water may be run to the sewer, washing is continued until the water removes nothing more from the cake. If the

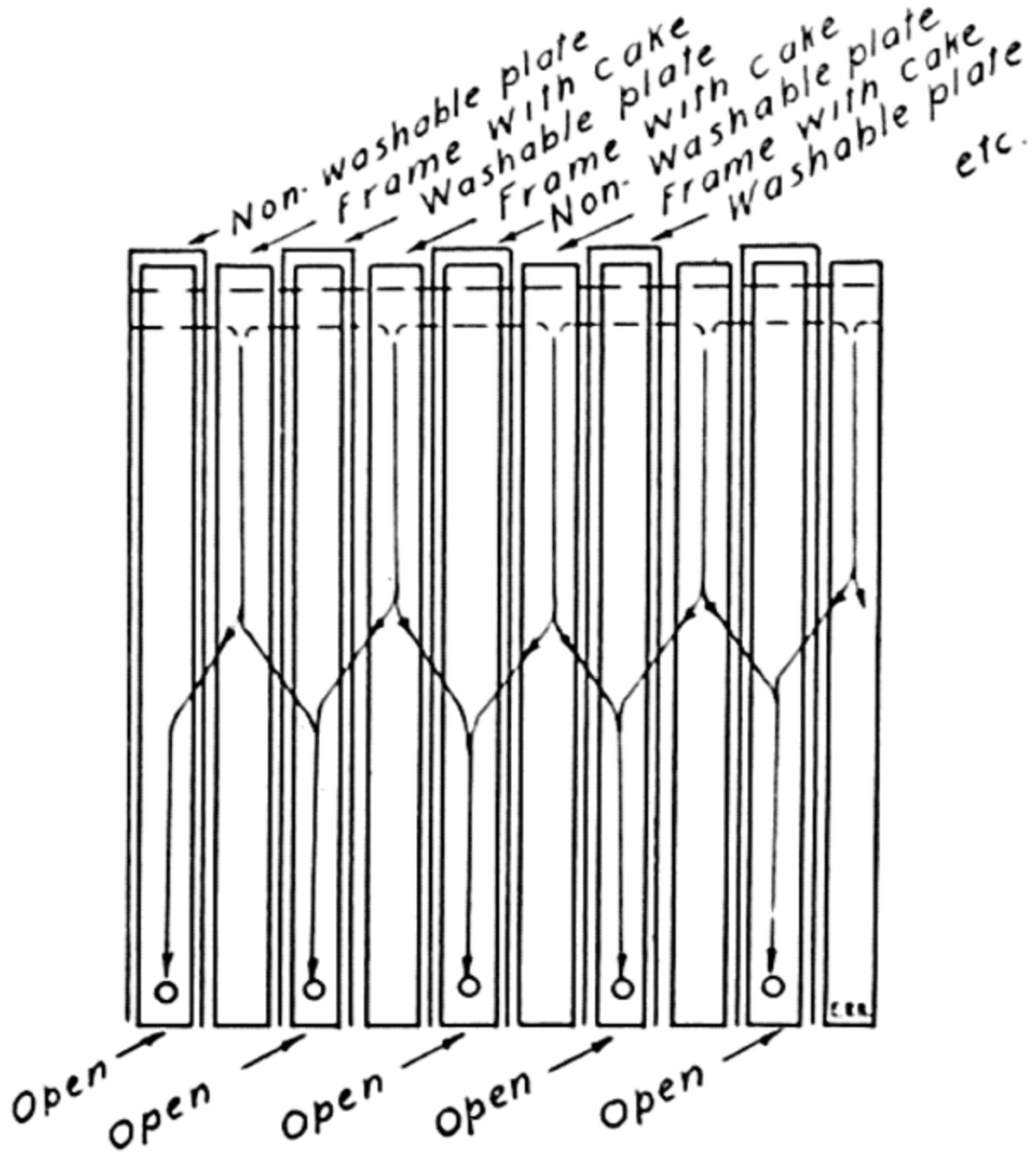


FIGURE 282.—Five plates and five frames when filtering.

cake is valueless, only so much wash should be collected as can be reused in the process without concentration, for only when the material is expensive will it bear the cost of fuel for the concentration of weak wash waters. After the washing is carried to the desired point, the press is opened, the plates and frames pushed apart and the cake in the frames dumped into a hopper in the floor, which leads to barrows, or carts, or a screw conveyor. The plates are pushed together again, the press closed, and it is then ready for the next filling.

Instead of a cart, the valueless cake may be flushed away without labor by running the chute to a tank with a stirrer, and feeding a strong flow of water with continuous overflow of muddy water to the sewer.

Good washing of the cake requires that it be not too high in solubles, for as these dissolve, the cake is weakened, and "rots"; as soon as one channel has formed all the water will flow through that, and there will be no washing. For that reason, a different procedure is sometimes used. A first filter-pressing removes the liquor, leaving a "strong" cake, which is not washed in the press. Instead, it is dumped into a tank with stirrer, and there made up with wash water from a later operation; the solubles are now

well dissolved, and this slurry is filter-pressed in its turn, and this time it is washed; the "weak" cake is so low in solubles that it will not rot.

A press with twelve plates and twelve frames each 12 inches square is a small press; one with 350 circular plates, 5 feet in diameter, is an unusually large one. In ordinary plant work, a press with 49 plates, each 3 feet square, and 50 frames 2 inches thick, is usual; such a press, fed with 20 per cent slurry, whose solids are low in soluble salts, will have a cycle of

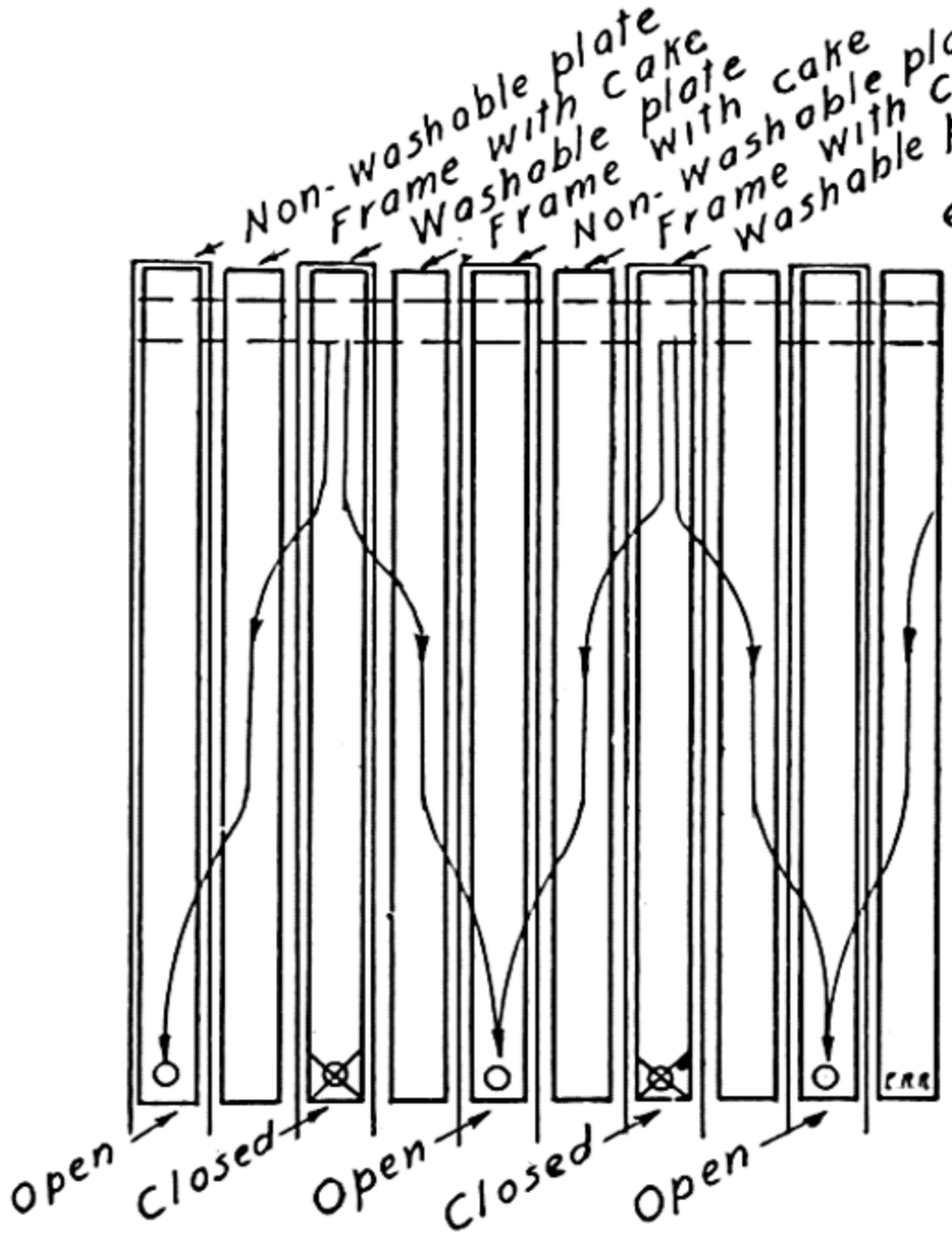


FIGURE 283.—Five plates and five frames when washing.

2½ hours; three-quarters hour to fill; one-half hour to wash, 1¼ hours to dump and close; it will dump 4000 pounds of mud. This figure will vary with the density of the cake, and with other conditions; it is given to indicate the duration and extent of such operations.

Cast-iron is the most common material, but wood is frequently required; other materials rarely. As indicated before, the plates may be circular as well as square. The frames may be thicker, 4 inches for example, so that they will hold more cake; 2-inch thickness is rarely exceeded if washing must be done. The plate and frame may be combined in one, giving the so-called recessed plate; many other modifications are on the market. Presses are usually opened and closed by hand, by means of a long bar turning the terminal screw which actuates the movable end piece; for very large sizes, mechanical power is used.

The slurry is forced into the pump by means of a duplex pressure piston pump, or a triplex plunger pump, or a blowcase whose principle of operation is similar to that of the acid egg. The pressure varies from 3 to 4 pounds at the start to as high as 40 pounds when the press is full.

The Shell-and-Leaves Type of Press. In this type of press, light wire frames bearing the filter cloths are provided, which fit in a steel shell; dur-

ing filtration, the slurry fills the shell, entirely surrounding the cloths; these become coated by the cake, while the clear liquor reaches the inside of the frames and runs off through a pipe connection at the base. In the Kelly press, one of the most successful representatives of this class, the

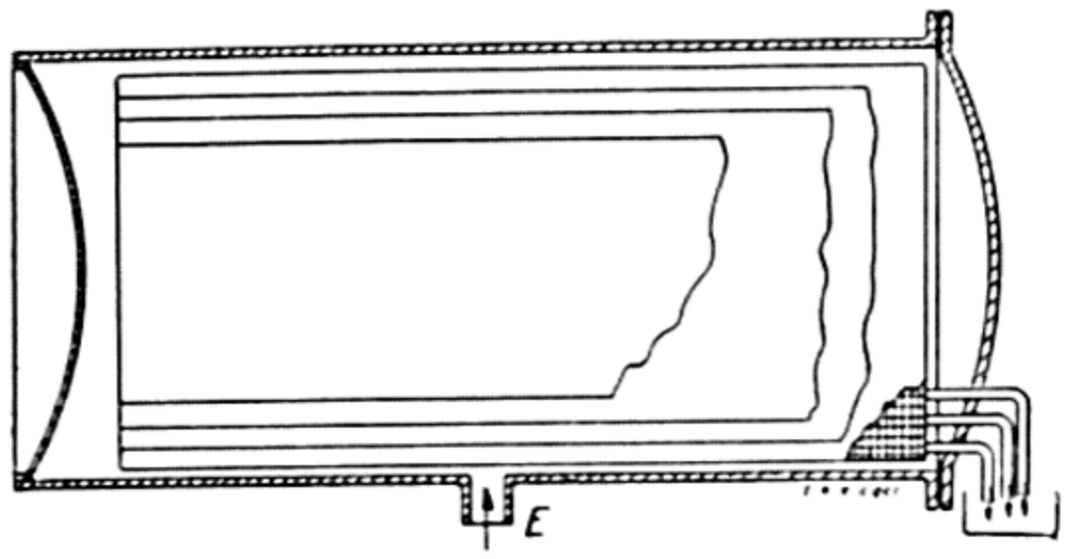


FIGURE 284.—Longitudinal cross-section of a 48 by 120-inch Kelly press, showing filter leaves and slurry inlet at *E*.

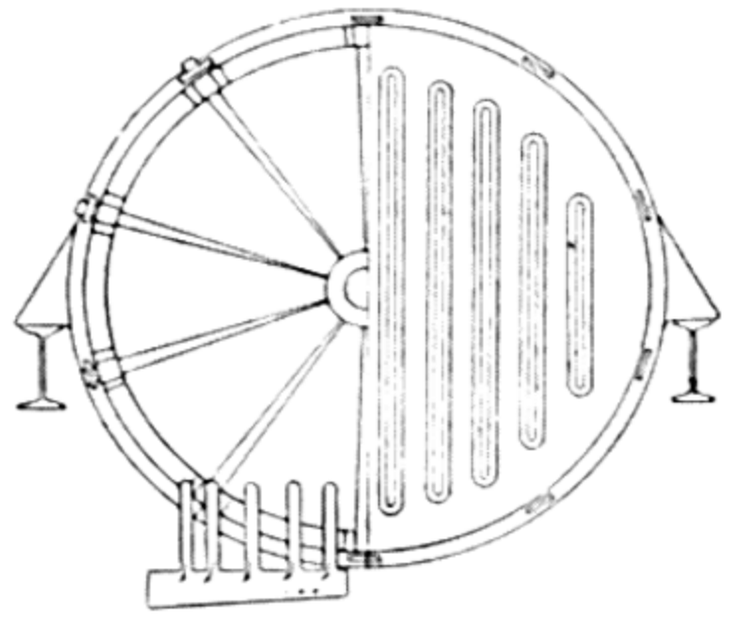


FIGURE 285.—Front view of the Kelly press, with one-half of the movable head plate removed to show the filter leaves.

leaves are rectangular, and are fastened to the cast-iron head; the shell is cylindrical, lying on its side. The leaves and cast-iron head are mounted on a carriage having four small wheels, which run on two rails set inside the shell and on the outside extension of the rails. After the desired thickness of cake has formed, the carriage is pulled out horizontally by chains actuated by a small compressed air motor, and the cake is dumped by jarring the frames with a long pole, aided by a stream of water from a hose. After the cake is dumped, the motor is started in reverse, the carriage is pulled in,

FIGURE 286.—Cross-section of a filtering leaf in the Kelly press, with cake on both sides, ready to be dumped.

and the press closes. The construction is made clearer by the three illustrations adjoined (Figures 284, 285, 286).

The main advantage of the Kelly press is the ease in dumping; the cake merely hangs onto the frames and is easily dislodged; the amount of hand labor is low. The slurry enters near the center of the shell at its base,

from a blowcase located on a lower floor; the filtrate runs out through cocks in the head of the press into a trough which delivers it to a dividing box set at the side, out of the way of the pulled-out carriage. On closing, the chains pull through a toggle joint which forces the head tightly in place and lock it by pushing stout steel bolts into the receiving hoops set in the shell.

If the cake must be washed, the slurry remaining in the shell after complete cake formation is run back into the blowcase, and water introduced. The progress of the washing is followed as it is in the plate and frame press.

Because of the ease of dumping, the cycle for the Kelly is short, and its capacity per day is high. A press 48 inches in diameter and 120 inches long will dump 4000 pounds of washed cake in 1½ hours, distributed as follows: three-fourths hour to build the cake, one-half hour to wash, and one-fourth hour to open, dump, and close the press. These values will vary widely with the percentage solids in the slurry, and with the permeability to water of the cake, and its density. The merits and defects of this press will be discussed after the third type, the automatic continuous suction filter, has been described.

The Sweetland press is another example of the shell-and-leaves type; in the Sweetland, the leaves are stationary, and the shell, which is divided in two halves horizontally, hinged together, opens jaw-like to allow the cake to be dumped.

The Stationary Suction Filter. The simplest type of suction filter consists of a two-compartment box, usually circular; a perforated plate over which the filter cloth is spread separates the two compartments. The slurry

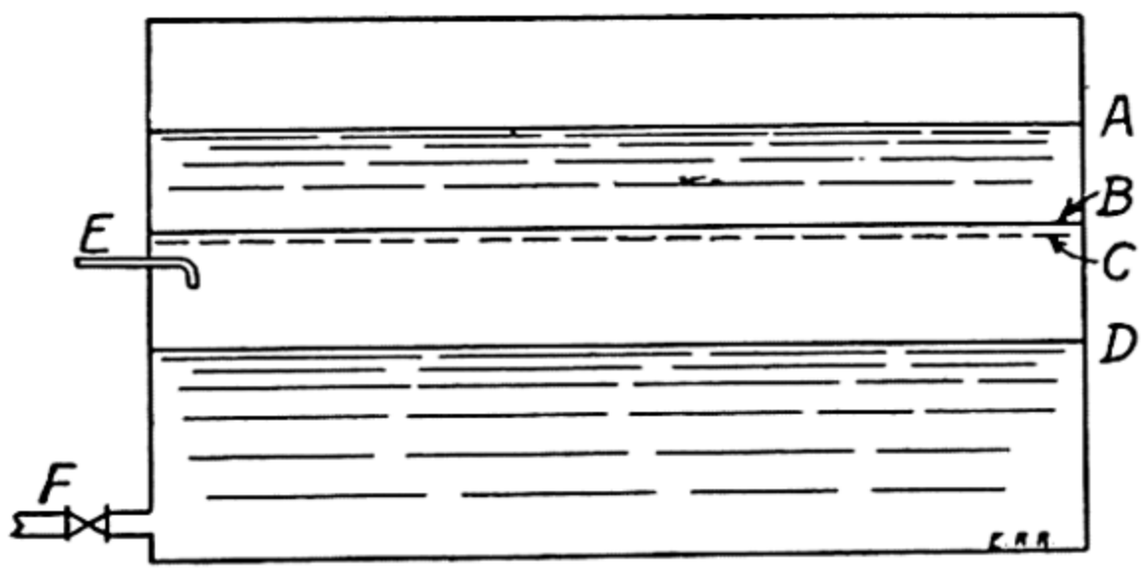


FIGURE 287.—Stationary suction filter; *A*, level of the slurry; *B*, filter cloth; *C*, false bottom; *D*, level of the clear filtrate; *E*, suction pump connection; *F*, liquor outlet.

is run on top of the cloth; the lower compartment box has two connections, the upper one for a suction pump, the lower one for running off the liquor; the suction pump is connected and the clear liquid passes into the lower compartment. When this is nearly full the suction is disconnected, and the filtrate run off through the lower connection. Usually the size is so proportioned that a batch of slurry may be filtered without interruption. Stationary suction filters of this type are constructed of lead, stoneware, or cast iron, and have been made as large as 6 feet in diameter. They give good service for slurries with a low percentage of coarse solids, such as a thiosulfate liquor containing some suspended sulfur. "Nutsch" is an old name for the stationary suction filter and is gradually going out of use in America.

The operation is intermittent; the liquor could be removed continuously by drawing it off as fast as it collects, through a separator, to which the

suction pump would be connected; the liquor would drop out into the closed separator. But this would not provide for the removal of the cake on the cloth; a shutdown every little while would be necessary in order to remove it. The more solid the slurry contains, the more frequent the interruption. This difficulty is removed in the rotary suction filter.

Another way to employ suction for filtration with intermittent operation is by using *filter leaves*, suspended in the slurry with suitable connections for the suction. The liquid passes through the covering cloth, while the mud coats the sides of the leaves. After this coating has reached a certain thickness, the leaves are lifted out by a traveling hoist or an overhead crane and lowered into a wash tank or re-slurry tank. The Moore filter leaves are so used in the Freeport plant (Texas) for collecting magnesium hydroxide from sea water.[1]

The Rotary Suction Filter, Drum Type. The rotary suction filter is automatic, and has continuous cake discharge, continuous filtration and

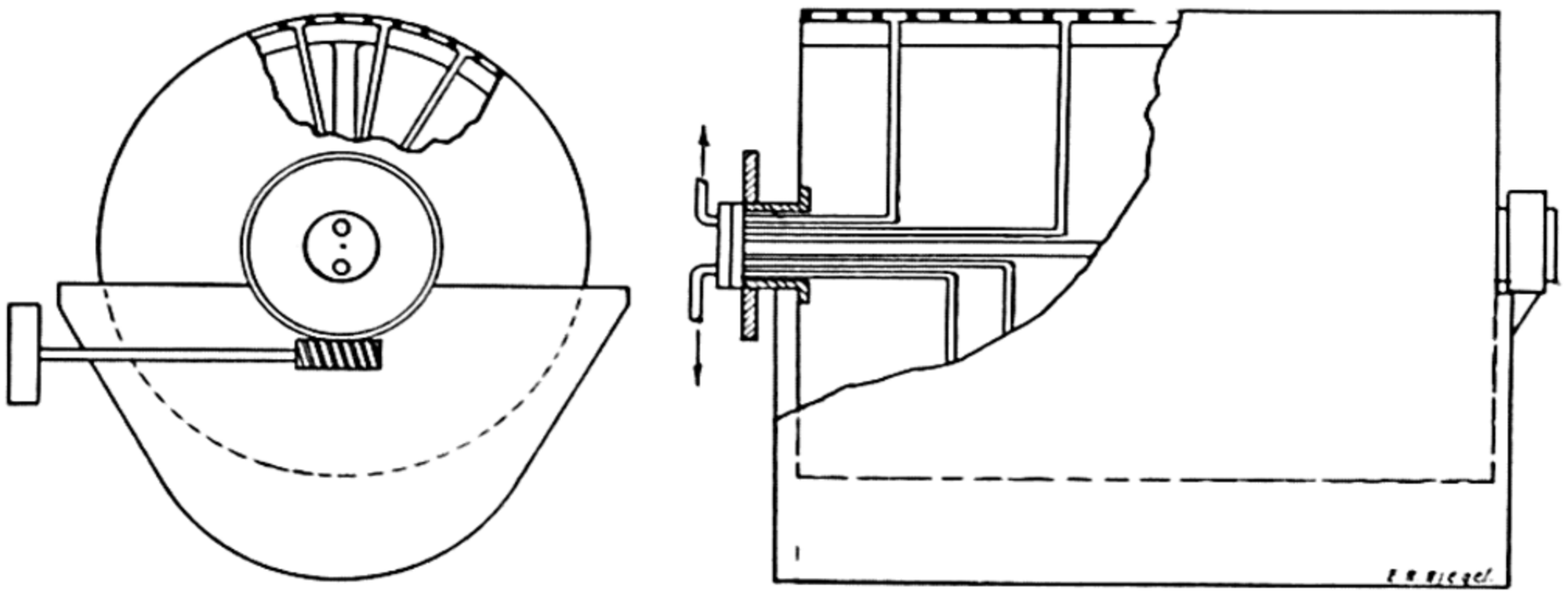


FIGURE 288.—The Oliver continuous suction filter; front and side view.

wash. One of the well-known examples of this type is the Oliver, which consists of a cylinder or drum lying on its side and carrying the filter cloth, of a knife or scraper for the discharge of the cake, of a tank holding the slurry, and of auxiliary apparatus such as pumps and receivers. The drum is mounted on a horizontal shaft carried by the slurry tank, and dips into the slurry to a depth shown in Figure 288; liquor is drawn in, and the surface becomes coated with cake; as the drum revolves the cake emerges and meets the wash water which is applied by a spray; as it revolves further, the washed cake meets the discharge knife. At the moment the cloth nears the knife, steam under pressure forces it out slightly, bulging it, causing clear scraping and clearing the meshes. The knife does not bear on the cloth, as that would wear it too fast, but on a wire wound over the cloth, spaced half an inch apart or so.

The simultaneous application of suction for the filtrate, suction for the wash water, and steam (or compressed air) for the blow is achieved by means of an ingenious mechanism, the circular valve. It consists of two halves, one of which rotates with the drum, while the other is held stationary

[1] *News Edition*, 19, 1213 (1941).

by the liquor lines; a stud set in the rotating half bears on a spring with loose collar which forces the stationary half tightly against the rotating half. The location of the valve is at the end of the shaft as shown in the illustrations. The surface of the drum consists of shallow wooden or cast-iron chambers 12 inches square, covered with sections of one-fourth-inch wire netting to support the cloth. Each chamber has a pipe connection to the valve, running first radially to the shaft, and from there through a main connection which unites the liquor from all sections lying along a horizontal, to a port in the rotating half of the valve. These ports form a circle; the stationary half of the valve has a circular channel fitting over this circle; the channel may be divided into compartments by means of small brass pieces (if the valve is brass). One such compartment would form the clear

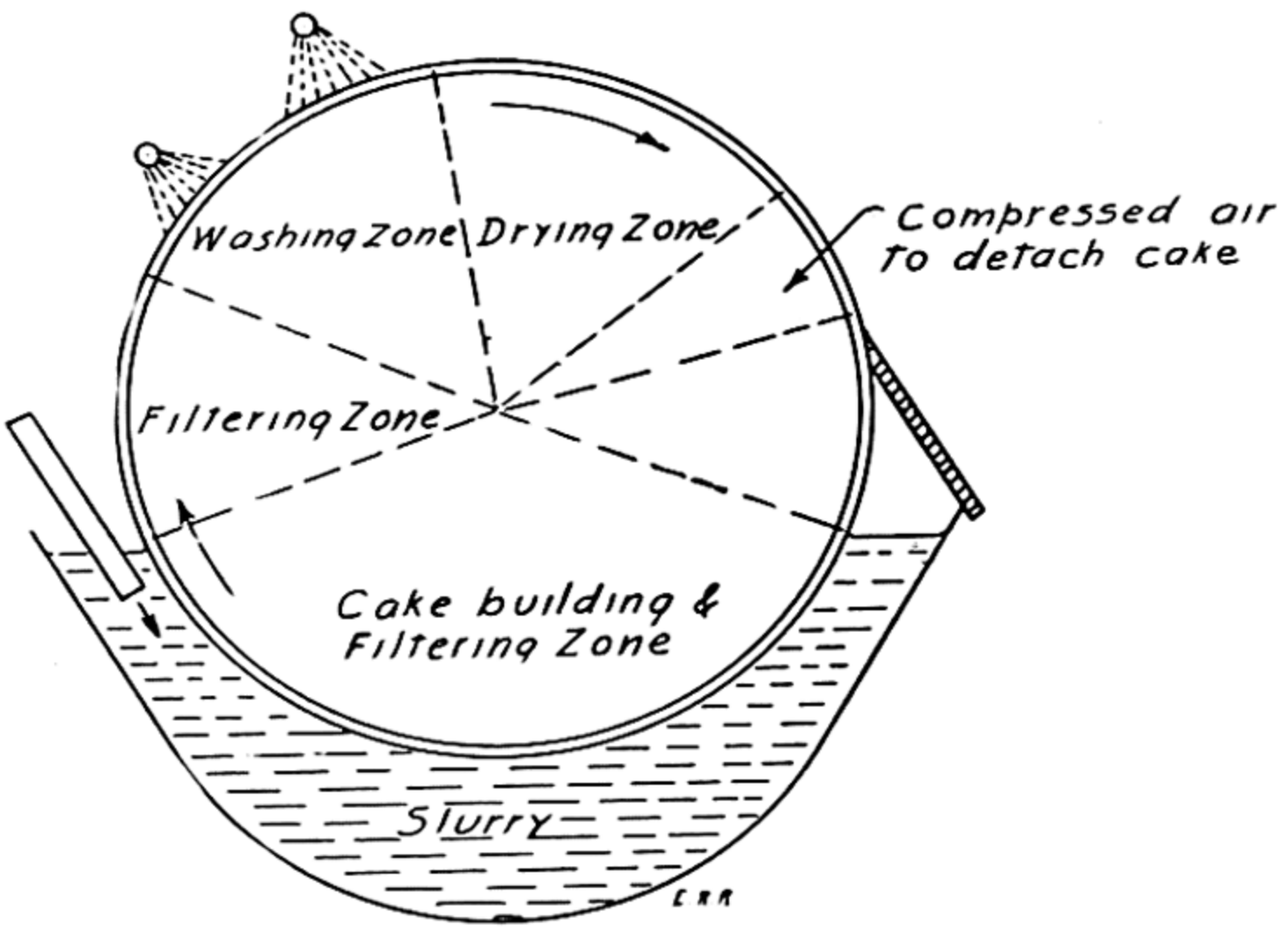


FIGURE 289.—Filtering drum of the Oliver continuous suction filter, showing the filtering, washing, drying, and blowing zones.

liquor compartment and communicate with the clear liquor line, the next would be the wash-water compartment, feeding the wash-water line; a very small compartment, fitting one port only, would bring the steam blow. Since the bridges are movable, the number of ports in connection with the clear liquor line may be varied; if increased, for instance, it would have the effect of bringing more drum surface under the action of the clear liquor line; if at the same time the submergence of the drum is increased, which is readily done by raising the level of the slurry in the slurry tank, it will mean a greater zone for cake building. The proper adjustment of the stationary half of the valve is made through a special valve rod.

The valve surfaces are machine-faced to give perfect surfaces; they are lubricated from two or more pressure grease cups; the wear is slight because the drum revolves once in 7 minutes, or similar speeds. Each port fits perfectly against the inset bridges, so that no internal leaks can take place. For alkaline liquors, the valve should be of cast iron.

A suction pump pulls out the liquor and any false air which has leaked in, to a separator, wherein the liquor drops to the bottom and is pulled out by a separate liquor pump, while the air rises and is removed by the

suction pump. The same suction pump serves for the wash water, but the suction is reduced by means of a reducing valve, for it is well that the filtrate be pulled in rapidly, but a definite period of time should be provided during which the wash water may remain in contact with the cake. The wash is pulled through a separator, from which the wash liquor is pulled out by means of a separate pump. A complete assembly is shown in Figure 290.

The cake is discharged by the knife onto an apron, and from there may be removed by a screw conveyor. The feed of the slurry to the tank, the drawing off of the clear filtrate, the application and removal of the wash water, and the discharge of the cake are simultaneous and continuous functions; if the cake is removed automatically, the filter is automatic; no labor of any kind is required. It has considerable flexibility, so that it may be adapted to a great variation of slurries. If the percentage of solids is high,

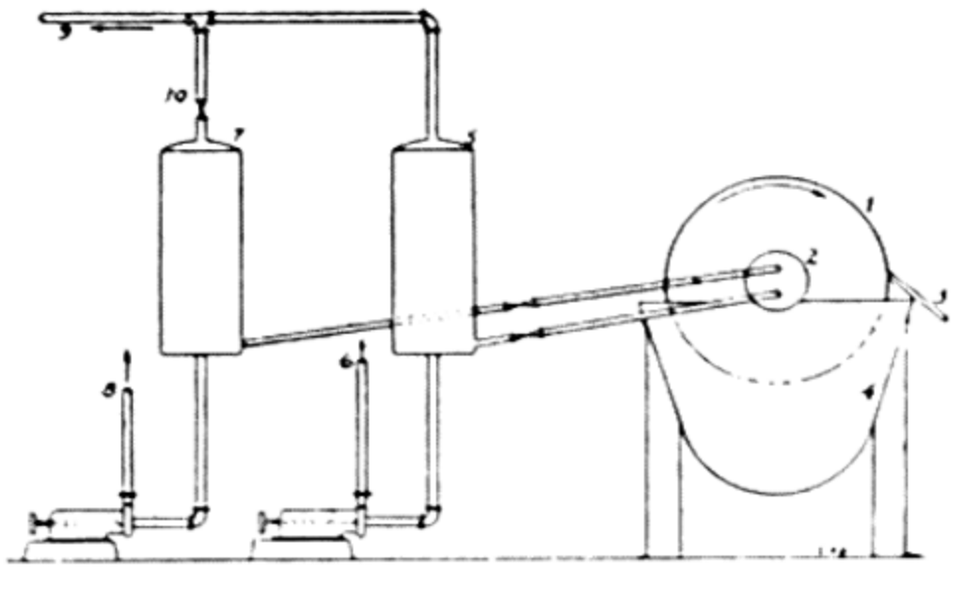


FIGURE 290.—Assembly for a small-scale Oliver suction filter; 1, filtering drum; 2, filter valve; 3, discharge knife; 4, slurry tank; 5, separator for filtrate; 6, liquor pump for filtrate; 7, separator for wash; 8, liquor pump for wash; 9, to the suction pump; 10, valve for reducing the suction on the wash area.

the drum revolves fast; if the percentage is low, the drum is made to revolve slowly; if no washing is needed, the submergence may be great; if washing is important, the wash zone is extended. The filter cloth is chosen from the wide choice of material for maximum service. It is no wonder that the automatic continuous suction filter has been very successful.

Its main limitation is that of pressure, since the atmospheric pressure, 14.7 pounds, is the maximum, and all of it is rarely applied. With volatile solvents which must be filtered hot, this type of filter fails, for the solvents volatilize, and no liquid at all, in the worst cases, can be pulled through the cloth. The difficulty is overcome by placing the filter inside a cylindrical pressure chamber. With concentrated, warm salt solution in water, the open filter functions well, if the temperature is not over 70° to 75° C.

Dorrco Filter. In the Dorrco filter, which is also a rotary suction filter with continuous operation, the sludge is contained within the drum, whose inner wall bears the filtering medium. The dewatered, washed cake is discharged into an inner trough. There is greater ease in filtration, in that the coarser particles settle out against the filtering cloth, with the finer ones drawn in only later; the plugging of the filtering cloth should be less likely. Another advantage in this novel design is that the drum can run on idling rolls.

Rotary Suction Filter, Disk Type. The American Continuous Vacuum Filter represents the disk type among the rotary suction filters. It is a well-known filter which has been established in plant practice for many years. The filtering medium covers flat disks which are mounted centrally

on a hollow shaft through which suction is applied to the under side of the filter cloth. The assembled shaft and disks are in turn mounted upon the slurry tank. The disks revolve with their lower portion in the slurry; as they emerge, the cake dries and wash may be applied. At the discharge point, just before entering the slurry again, small rollers remove the cake which can drop downward because at that place the slurry tank is deeply notched. The suction pipes from the various disks terminate in the rotating part of the valve, while the stationary part carries the liquor and wash lines. The valve is faced and not flat, but of the conical plug type which possesses the

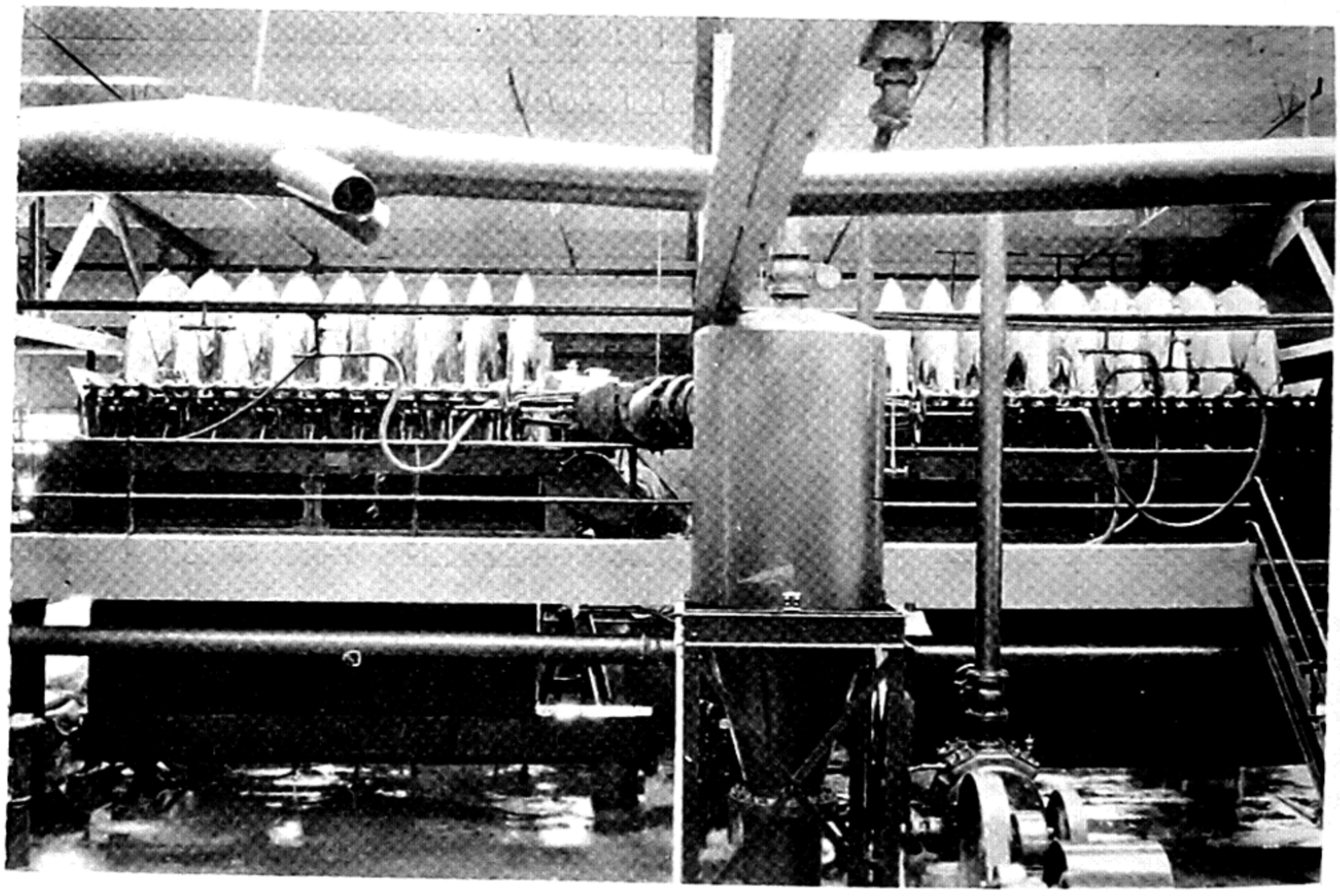


FIGURE 291.—Twin unit of an American Continuous Disk Suction Filter, showing two 9-disk units, separator and pump, as well as conveyor box on the floor of the filter cake. (Courtesy of the Oliver United Filters.)

important advantage of seating itself as a slight wear takes place. This filter requires auxiliary devices such as the drum type suction filter does, separators, suction pump and liquor pump.

The Continuous Pressure Filter. The limitation of pressure has been removed by the development of the continuous pressure filter, which resembles the suction filter, but has a casing over the drum in addition, so that pressure above atmospheric may be applied; also a closed box for the screw conveyor and a receiver for the cake must be provided. A well known example is the Vallez filter. The suction filter will continue to be used whenever possible, since it is simpler; in special cases the pressure filter will have to be substituted.

The Cuno filter is an edge filter; the dirty liquid must travel past the edges of horizontal circular plates packed close together, to reach the central outlet passage. The dirt is deposited on the upper surface of each disk.

The Cuno filter is self-cleaning, by manual operation, and is thus adapted to continuous operation.

For the removal of a small amount of suspended solids the so-called "mass filter" or pulp filter (Kiefer) serves well. The cloudy liquid travels through thick disks of wood pulp or other masses, which retain the solids, and deliver a brilliant filtrate. The beer filter is of this type. Another device employs a napped blanket-like cloth, successfully applied to the clarification of syrups in the beverage industry.

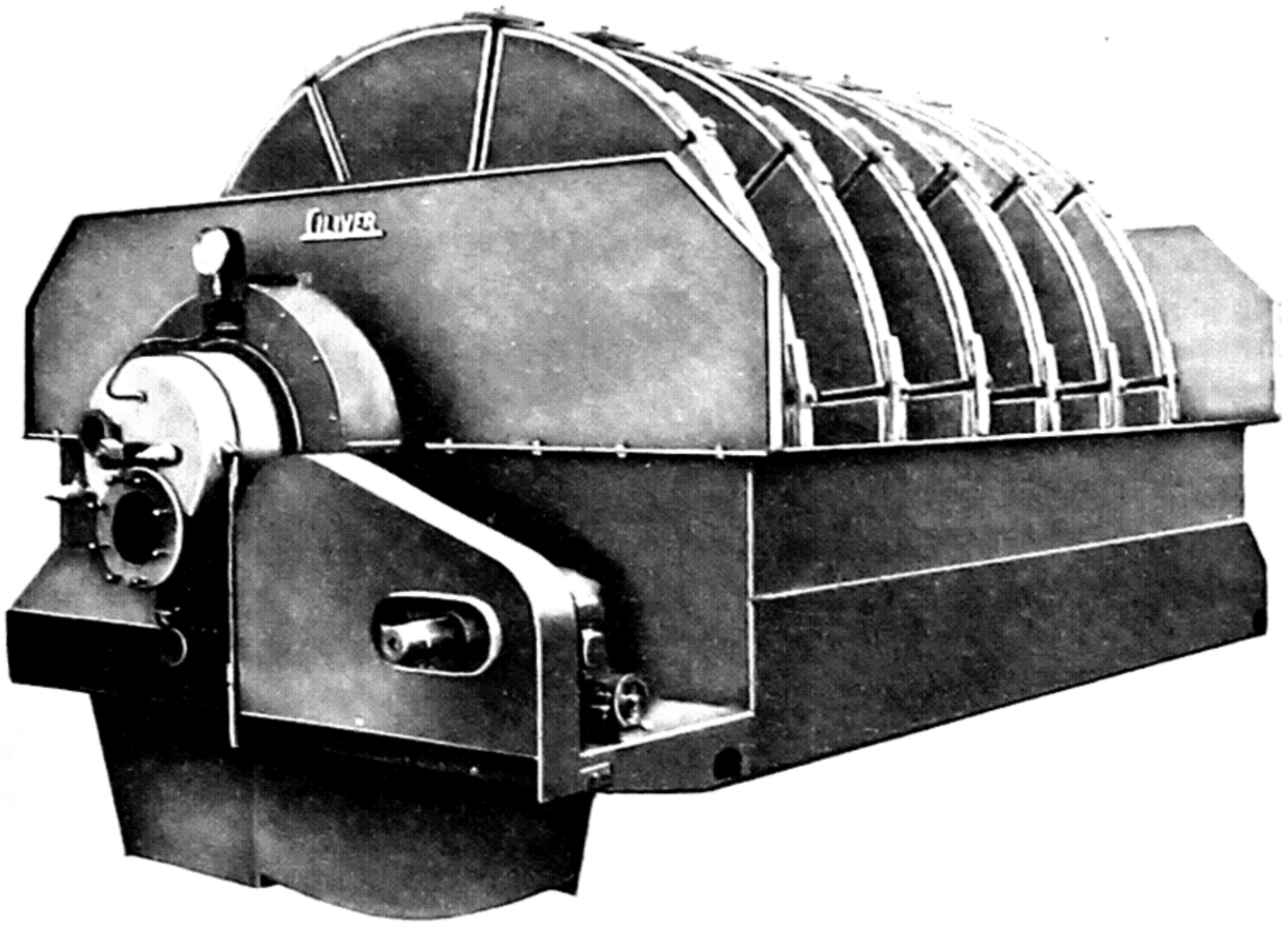


FIGURE 292. — American Continuous Vacuum Drum Filter, Disk Type.
(Courtesy of Oliver United Filters.)

Comparison of the Several Filters. On closer study, it will be found that every filter has its field which it serves better than any other; the various types supplement each other. The plate-and-frame press is the proper device for a process requiring one dumping a day or in several days, for then the press may be put together with care; the surfaces cleaned to give tight joints. For a cake which is valuable, so that the dumping is a cautious operation, there may be several openings per day and yet this press may be the best choice. But for a valueless cake, in a press worked to capacity, opened five or more times per nine-hour day, the press may be closed carelessly, especially if it is of large size. To bring the plates together, 100 plates or frames will have to be pushed along the two horizontal bars; unless these are clean and well oiled, the press will not be tightly closed. Unless the frames and plates are absolutely free from grit, the surfaces will not meet and there will be a leak; even if the leaking liquor is recovered, and sent

back to the press, it is a waste of filtering capacity. Every joint between plate and frame is a potential leak, hence in a 50-frame press there are 100 such possible leaks. In this respect the Kelly press is greatly superior; it has one gasket, hence only one possible leak; to keep one gasket clean is a reasonable task, and as a result, it rarely leaks. The Oliver has no possibility for leaking except in the valve, and that is easily refaced.

The plate-and-frame press has a valuable feature in that the filtrate is visible; should one plate run dirty, it may be shut off and the filtration continued with the remaining plates; the Kelly press has the same valuable feature; in the Oliver, it is missing; if there is a break in the cloth so that mud enters, there is no way of detecting the faulty place, and all the filtrate is slightly muddy. The blow of steam or compressed air cleans the cloth too well, in some cases, so that the fine layer of mud must reform, and while it does, the liquor runs slightly muddy. This constitutes a fault in the Oliver which is absent in the other two filters. If a slight turbidity does not matter, the great economy of the Oliver and similar suction filters will place it first; but if absolute clarity is required, the older presses are superior.

Both Kelly and plate-and-frame presses suffer from the fact that their operation is discontinuous; in that respect the automatic suction filter and the automatic continuous pressure filter are supreme.

Strictly speaking, filtering and washing mean a separation of the insolubles from the liquor, followed by a displacement by water of the liquor adhering to the solid. A good example is the ferric hydrate and lime mud in the solution of sodium sulfate. More than that should not be required from the filter, yet frequently more is. Thus when the cake contains salts in the solid state, it will be expected that they will be dissolved during the "washing," but "rotting" of the cake will occur. This will have serious results especially in the Kelly press, because its cake is unsupported, and when the structure is weakened by the removal of salts, the cake drops off into the shell, clogging the inlet and otherwise interfering with smooth operation. Another slight drawback to the shell-and-leaves type press is the necessity of running back to the blowcase a shellful of slurry once the cake has reached the proper thickness, before the press can be opened.

The centrifugal basket is also a filtering device, and very successful; because it is primarily a means of rapidly draining a wet solid, it is described under that head in Chapter 43.

In first cost, the plate-and-frame press is the lowest; its operating cost is the highest, but if the slurry is low in solids, requiring infrequent openings, it remains the most economical device. For the rapid handling of cake rich in solubles which need not be washed in the press, because the mud after dumping is reslurried, the Kelly or Sweetland will give excellent service. For a mud which must be washed with so much liquor that continuous operation is desirable, the rotary automatic suction filter, either of the drum type, or the disk type, is indicated.

Other Patents

U. S. Patent 1,870,485, multiplex rotary drum filter; 1,859,282, continuous filtering apparatus for removing clay, fuller's earth or other fine material, from oil; 1,799,768,

dual fluid filter using two filter media; 1,812,773, a filter for filtering suspended solids from liquids, consisting of a vertical, tapered tube filter press.

Problems

1. A Kelly press dumps 4000 pounds of cake once in 2½ hours, with one man operating the press. A plate-and-frame press dumps 4000 pounds in 2½ hours, requiring two operators. What is the figure for hours of labor on the basis of one individual (called man-hours) per 1000 pounds of cake? Inspection and repair labor is left out of consideration. If the Oliver is completely automatic, what will its man-hour figure be? Make a table comparing the three values.

2. An Oliver filter drum 4 feet in diameter and 6 feet on the face makes 1 revolution in 6 minutes. What is the circumferential speed? In order to raise the circumferential speed by one-half, how much faster must the filter revolve? How many square feet of surface has the drum?

3. Thirty-two thousand pounds of wet cake are dumped per 10-hour day from 8 plate-and-frame presses. If each frame holds 80 pounds of wet cake, how many frames has each press?

4. A slurry carries 10 per cent of insoluble mud, on the dry basis, that is, determined dry. How many pounds of liquor form while 10,000 pounds of cake are collected in the presses? If the density of the filtrate is 1.44, how many cubic feet of liquor are collected? If the density was 1, it would take 62.5 pounds for 1 cubic foot. How high would the filtrate liquor stand in a circular tank 12 feet in diameter? It is assumed that all the liquor is forced out of the cake and collected; this is very nearly, but not quite, realized by blowing the cake with steam.

Reading References

"What is the most suitable filter?" D. R. Sperry, *Chem. Met. Eng.*, **31**, 422 (1924).

"Industrial filtration," Arthur Wright, New York, Chemical Catalog Co., Inc., 1923.

"The enclosed continuous filter," J. F. Wait, *Ind. Eng. Chem.*, **18**, 295 (1926).

"Principles of chemical engineering," Walker, Lewis, McAdams, and Gilliland, New York, McGraw-Hill Book Co., Ch. 11, 3rd ed., 1937.

"Filtration equipment in to-day's industry," H. J. Runyon, Jr., *Ind. Eng. Chem.*, **19**, 681 (1927).

"Studies in filtration, I—Critical analysis of filtration theory," R. F. Ruth with G. H. Montillon and R. E. Montonna, *Ind. Eng. Chem.*, **25**, 76 (1933); and "II—Fundamental axiom of constant-pressure filtration," *ibid.*, **25**, 153 (1933).

"The continuous centrifugal and some of its applications," E. M. James, *Trans. Am. Inst. Chem. Eng.*, **26**, 224 (1931).

"The separation of solids from liquids, thickening," Wm. Cullen and H. T. Durant, *Trans. Inst. Chem. Eng. (London)*, **12**, 210 (1934).

"Fundamental principles of industrial filtration," P. C. Carman, *Trans. Institution of Chemical Engineers (London)*, **16**, 169 (1938), with a bibliography of 179 titles.

"Attempt to derive general expression for rate of washing filter cakes," F. H. Rhodes, *Ind. Eng. Chem.*, **26**, 1331 (1934).

"An analysis of recent filtration equations—Filtration at constant pressure," M. G. Larian, *Trans. Am. Inst. Chem. Eng.*, **35**, 623 (1939).

"Filter media," F. J. Van Antwerpen, *Ind. Eng. Chem.*, **32**, 1580 (1940).

"Filter rates of clay-oil slurries," H. H. Bible, M. A. White and J. W. Donnell, *Ind. Eng. Chem.*, **31**, 1007 (1939).

"Evaluating filter aids." Richard N. Cogger and Harvey M. Merker, *Ind. Eng Chem.*, **33**, 1233 (1941).

"Theory and Practice of Filtration," G. D. Dickey and C. L. Bryden, New York, Reinhold Pub. Corp., 1946.

In the course of the growth of the chemical industries, a number of appliances have been devised which are characteristic of these industries. Their application has become great enough so that engineering firms devote themselves not only to a single type, such as evaporators, but to the best design of the evaporators for specific industries, for example, evaporators for beet-sugar liquors, or milk, or glucose concentration.

Chapter 43

Appliances Used by the Chemical Engineer

III. Evaporators, Dryers, Cottrell Precipitator, and Others

Among the appliances which have been perfected to a high degree of efficiency are the evaporators, whose heat source is usually steam; the most economical form, the triple-effect evaporator, reduces the fuel consumption to almost a third. The concentration of a dissolved salt yields a liquor which on cooling deposits crystals; these are separated from adhering mother liquor on a drain board, or more rapidly in a centrifuge. In many cases the substance must be absolutely dry, and this may be done in cabinet driers, vacuum driers, or most economically, in a rotary drier. Crystallizers and dryers are important appliances.

An appliance not far removed in form and in principle from the type of drier known as the drum dryer is the chip machine, which permits the rapid production of many substances in the form of thin chips which possess properties making them much superior to lumps.

The dust collector, the Dorr thickener, and mixers for pasty solids are frequently indispensable.

An electrical appliance which the chemical engineer uses freely is the Cottrell precipitator for dust and mists.

Evaporators. The simplest kind of evaporator is the open kettle hung over a fire, or the open pan, in the path of waste heat gases. Heating by means of steam, either in coils or in a chest with numerous horizontal or vertical tubes placed in the liquor is the usual practice; the vessel is closed, except for an outlet for the steam rising from the liquor, and this outlet may be closed by a valve. The use of steam in the coils permits a closer regulation of temperature, and the closed vessel allows the transfer of the contents to an elevated point by applying compressed air, on the principle of an acid egg. The single evaporator, working at atmospheric pressure, is largely used for the concentration of a solution which remains clear while in the evaporator, and deposits crystals only as it cools after transfer to the crystallizers; for such cases, the steam chest may be placed near the bottom. In the case of sodium chloride, there is a separation of the solid as the evaporation progresses, and it accumulates at the base of the vessel, in the conical part provided; the salt in the cone is more or less undisturbed, because the steam chest is situated well above it. For such a case as glycerin from a soap kettle, the concentration is performed at reduced pressure; the salt is removed at intervals without interrupting the evaporation,

by the aid of a salt box which is also under suction; by closing the valve at the base of the cone, the salt box can be emptied, then closed again, and evacuated, when it is ready to receive another salt dump.

For a number of products, the fuel item is so important that the triple-effect evaporator is used; familiar cases are the salt (NaCl) and the sugar industries, particularly beet sugar. The triple-effect evaporator depends upon the fact that the boiling point of any liquid in a closed vessel from

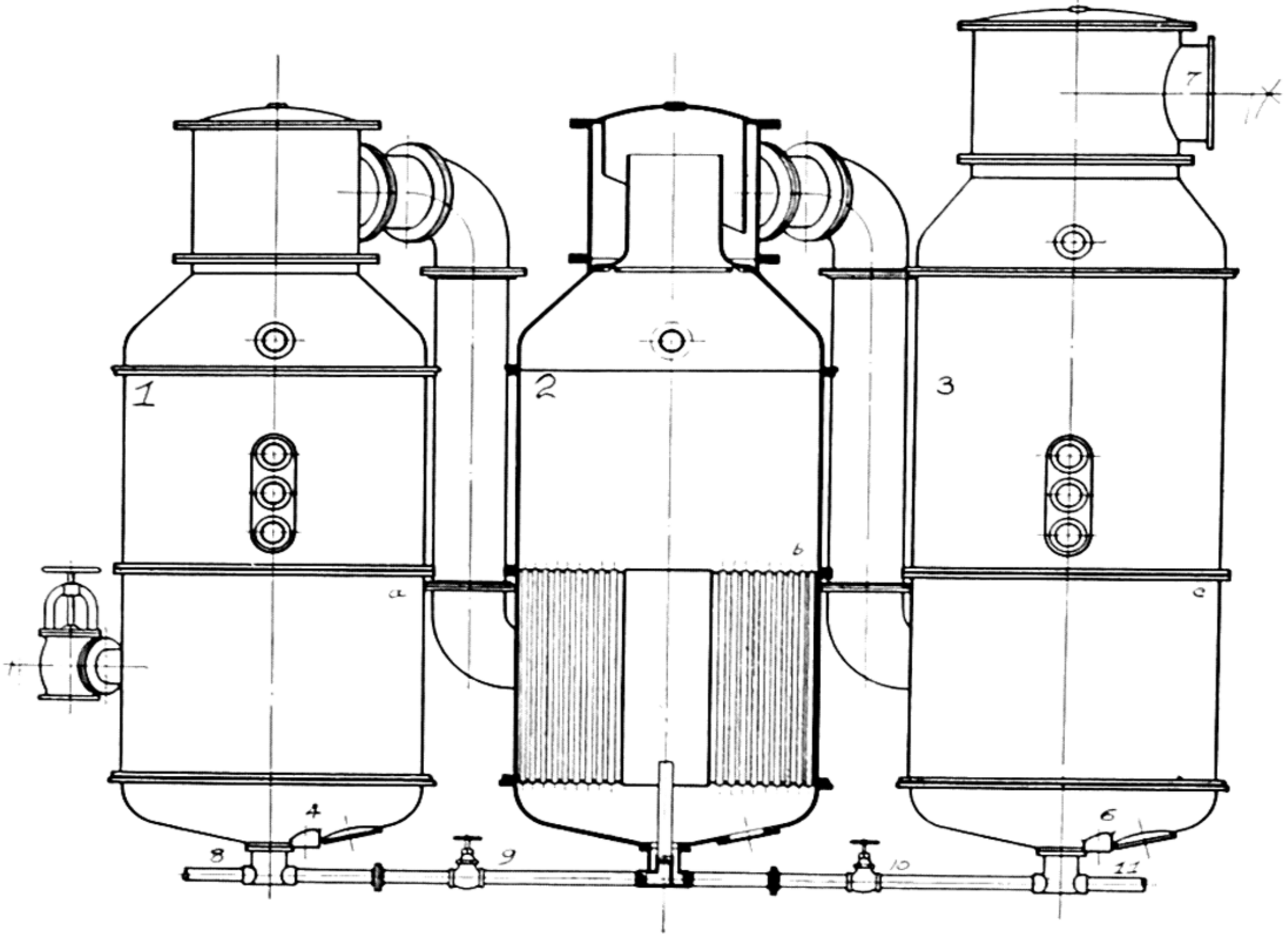


FIGURE 293.—Sketch of a triple-effect evaporator. Boiler steam enters steam chest *a*, with outlet 4 for condensed water; the steam from solution in No. 1 enters steam chest *b*; the steam from No. 2 enters steam chest *c* with outlet 6; the steam from No. 3 goes via 7 to condenser. The reduced pressures are given in the text. The weak solution enters No. 1 at 8; after concentration, it passes from No. 1 to No. 2 through 9, and after further concentrtaion from No. 2 to No. 3 through 10. The concentrated liquor leaves No. 3 through 11, periodically. (Courtesy of the Geo. L. Squier Manufacturing Co., Buffalo, N. Y.)

which the atmospheric air has been removed is lower than in the atmosphere, and furthermore, the lowering in the boiling point is roughly proportional (not absolutely) to the lowering of the pressure. The normal atmospheric pressure at sea level is 29.92 inches of mercury; the vacuum in the various vessels is expressed in inches of mercury which are forced upward by the air pressure against the pressure in the evaporator; an absolute vacuum is shown by a column 29.92 inches high, since then the pressure inside the vessel is nil.

The connection between the several effects is shown in Figure 293; the vapor from the central plant enters the first steam chest and causes the liquor to boil. The steam from this liquor passes to the steam chest of the second vessel, where it becomes the source of heat; after giving up its heat to the colder liquid it is liquid water, which is trapped off at the outlet from the chest. The steam arising from the liquor in the second vessel becomes the heating steam in the third chest; the water vapor rising in this third vessel passes to a condenser, where cold water returns it to the liquid state. An example from the concentration of sugar solution follows[1]:

	Vessel 1	Vessel 2	Vessel 3
Vacuum	2½ inches	14½ inches	26 inches
Temperature of entering steam	220° F. →	205° F. →	183° F.
Temperature of boiling liquor	205 →	183 →	130 → condenser
Temperature fall in each vessel	15	22	53

The same quantity of heat raises steam three times, and the saving in fuel is almost two-thirds. There is a consumption of steam running the suction pump; theoretically, it is only such as is required to pump out the vessel to the required pressure; practically, the pumping must be continued throughout the evaporation, because some air leaks in, and the liquor gives up dissolved gases, but even so, the steam consumed for the pump operation is very small, and the fuel consumption is cut nearly to one-third. There is an additional advantage in that boiling at low temperature gives a better product. Double effects and quadruple ones are also used[2]; more than four effects are rare.

For such an inexpensive product as salt (NaCl), the saving in fuel is most important, and triple and quadruple effects are commonly used in salt plants. They are of special construction, with conical bottom ending in a rising boot which permits constant discharge; in point of size, the evaporators for salt are probably the largest, as large as 30 feet diameter. The 20-foot diameter pan is quite common, with an over-all height of 50 feet.

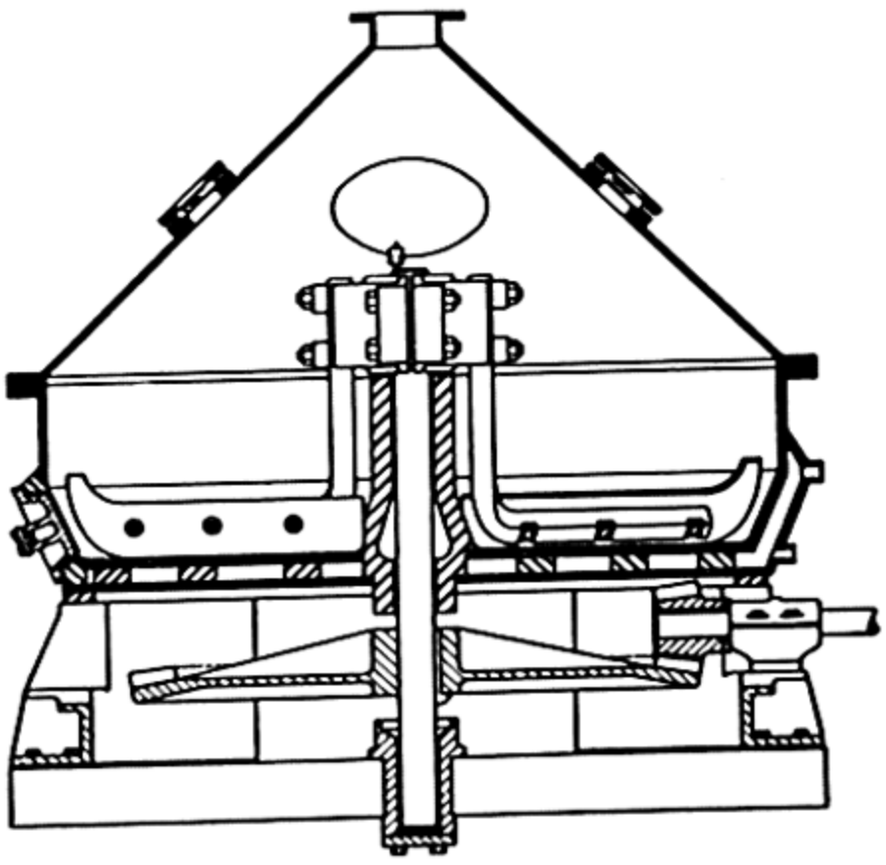


FIGURE 294.—Jacketed crystallizer with rotating arm, for the production of small crystals. (Courtesy of Buflovak Equipment Division, Blaw-Knox, Pittsburgh, Pa.)

[1] "The manufacture of sugar from the cane and the beet," T. H. P. Heriot, New York, Longmans, Green & Co., 1920, p. 259.

[2] An example of quadruple-effect operation will be found in *Ind. Eng. Chem.*, 10, 195 (1918).

The material is usually steel, but at least one triple effect for salt is of copper lined with tin.[3]

For sugar solutions, the liquor in the first pan is pumped to the second pan, there to be evaporated further; while in turn, the liquor from the second pan is pumped to the third pan, for still further concentration. In the salt plants, each effect receives brine of the same strength; the fuel saving is realized in either case.

Not only solutions of solids, but of high-boiling liquids are concentrated in single- or multiple-effect evaporators. A single vessel operating under greatly reduced pressure, and receiving, usually, highly concentrated solution from preceding evaporators, is called a vacuum pan.

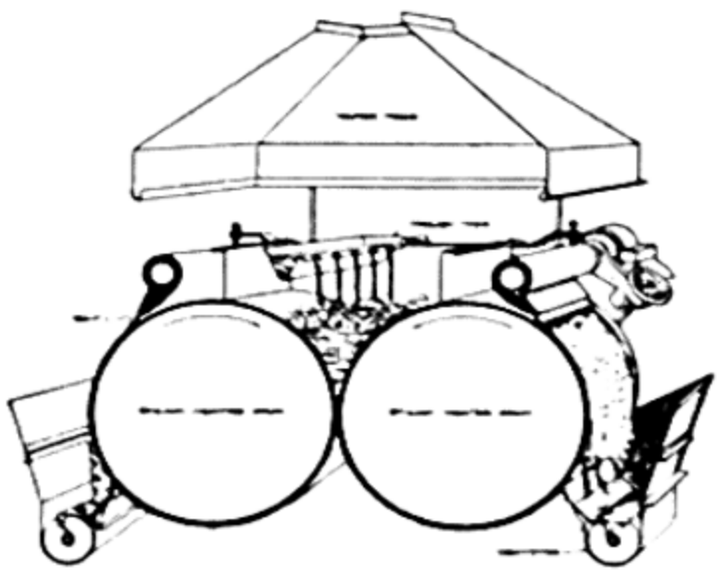


FIGURE 295.—Atmospheric double drum dryer, with liquid feed. The slowly revolving hollow drums are steam heated. The dry coat is scraped off as shown; each collecting box has a screw conveyor. (Courtesy of the Buflovak Equipment Division, Blaw-Knox, Pittsburgh, Pa.)

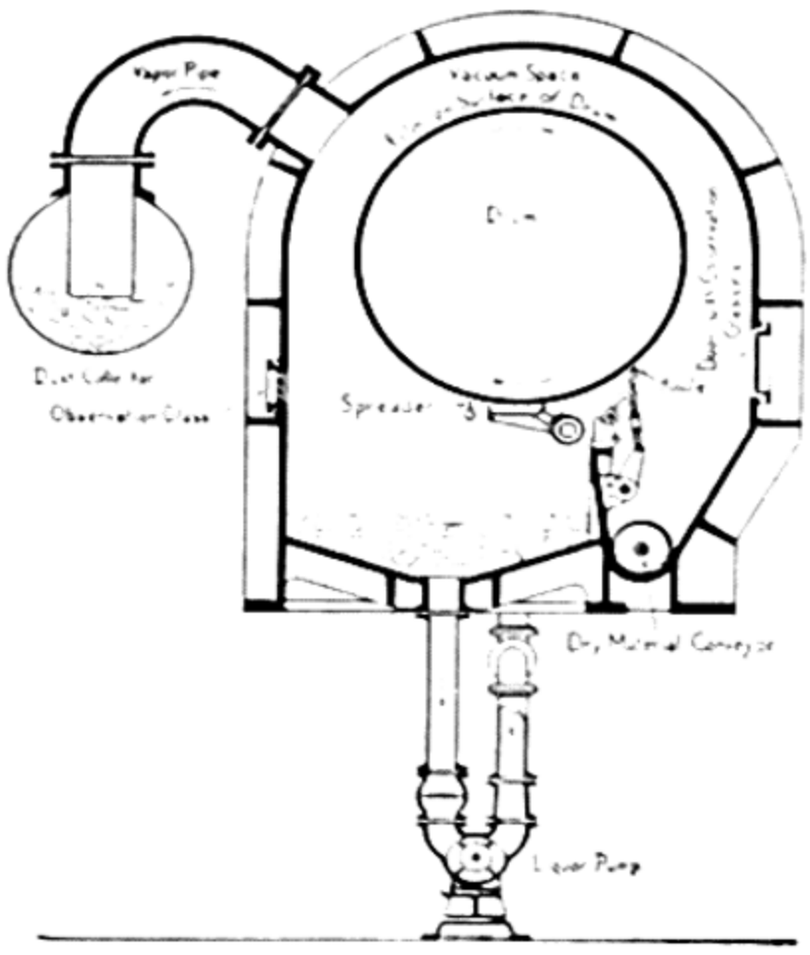


FIGURE 296.—Cross-section through a vacuum drum dryer. The suction is applied to the dust collector, just behind the vapor line. The 2 boxes for the dried material not shown. The slurry is pumped to the small trough next to the spreader, and constantly overflows. (By courtesy of Buflovak.)

Single, double and multiple-effect evaporators are now very generally built with the heating element separate from the vapor chamber, and with vertical tubes (generally) for rapid circulation. So desirable is it in many instances to have very rapid circulation, with the resulting short period of contact with the heating tube, that a pump is provided under the vertical heating element to drive the liquid still faster through it; such devices are designated as evaporators with forced circulation.

The important study of fractionating columns for the separation of liquids by taking advantage of the differences in their vapor pressure has been touched upon in Chapters 20 and 24. In the reading references, there

[3] *Bur. Mines Bull.* No. 146, W. C. Phalen, contains numerous illustrations of multiple-effect evaporators for salt (1920).

will be found grouped together valuable articles, which will afford the beginning of a scientific study of fractionating columns.

Crystallizers, Drain Boards, Centrifugals. The liquor from the evaporator, after suitable concentration, is blown, or pumped, to shallow vessels, of steel if possible, or wood or lead-lined wood, if necessary, where it deposits crystals on cooling. As a rule, the liquors are at rest; for the production of small crystals, a circular pan with slow agitation by a rotating arm is used, and by jacketing the pan, the temperature may be controlled. After

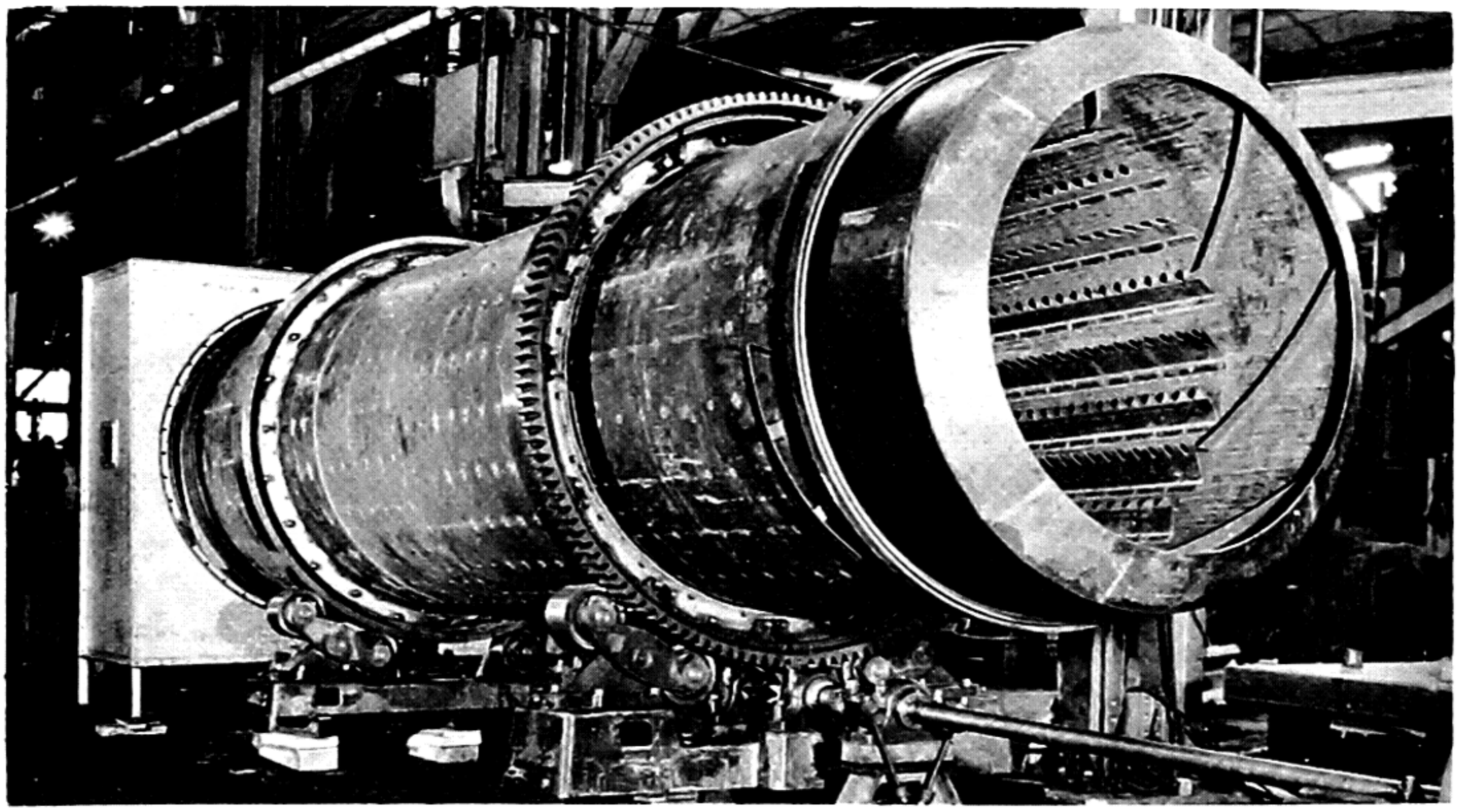


FIGURE 297. — A rotary drier with the feed end box, heating coils and fan removed. The longitudinal lifts, which are serrated, raise the material and drop it gradually into the current of warm air. The discharge end is at the left. (Courtesy of The Squier Corporation, Buffalo, N. Y.)

crystallization the mother liquor is run off, and the wet crystals may be piled on a drain board which slopes toward the crystallizer; a more rapid way of removing adhering liquor is by dumping the crystals into centrifugals, and after the proper charge has been added, setting the basket in motion; the mother liquor is whirled off and is caught in a circular apron. The modern centrifugal is driven from overhead, by direct-connected motor, and has an annular ring in the base which can be lifted for discharge through the bottom. A conveyor belt travels underneath and conveys the crystals to the screen, or dryer. The continuous crystallizers consist of several interconnected horizontal jacketed tubes in which a scraper moves the deposited crystals forward.

Dryers. Moist solids may be dried on trays placed in a closet, with a few steam coils at the base. A cabinet dryer is a closet with trays, fitted with a motor-driven fan and suitable partitions so that the air is circulated;

steam coils raise the temperature of the air to the desired point. Vacuum dryers are tray driers [3a] in strong iron boxes which may be evacuated; the trays stand on shelves which are hollow, and in which heated water, steam at various pressures, or oil heated still higher, may be circulated, so that a wide range of temperature is possible.[4] The rotary dryer is gaining on all other forms, however, because of its labor-saving feature, except for small-

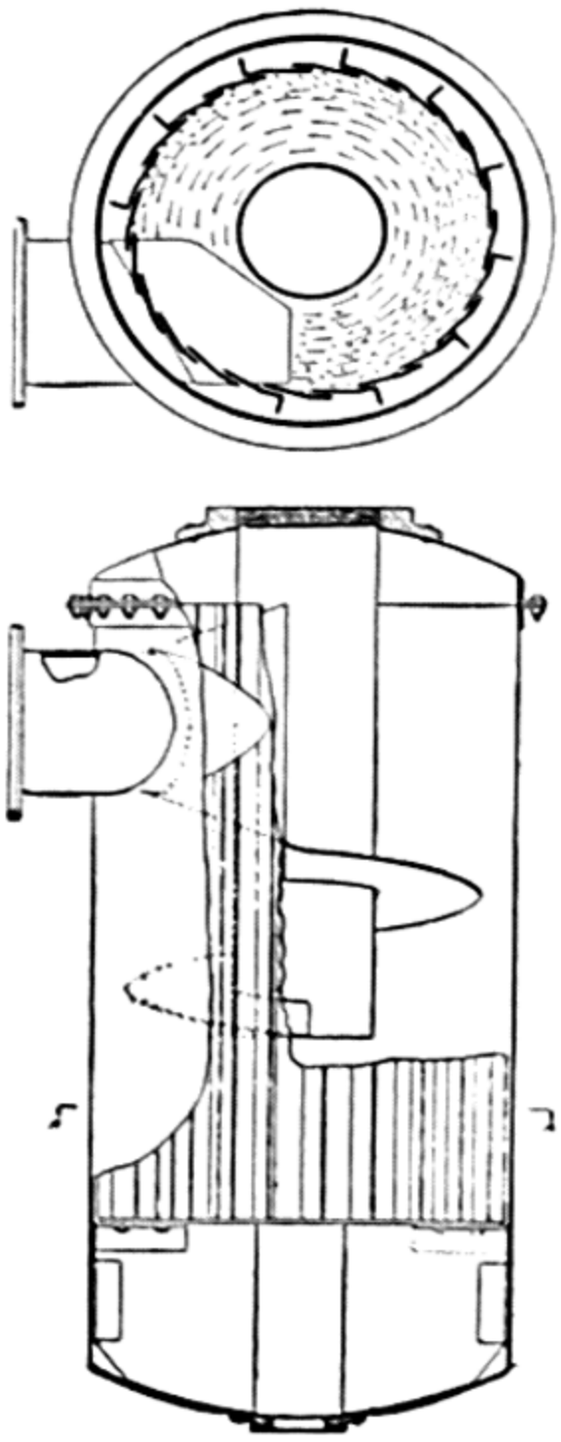


FIGURE 298.—Flick centrifugal catchall and entrainment separator. Entrained droplets pass through the slits of the inner wall, out of the path of the vapor or gas. (Courtesy of Wurster and Sanger, Inc., Chicago.)

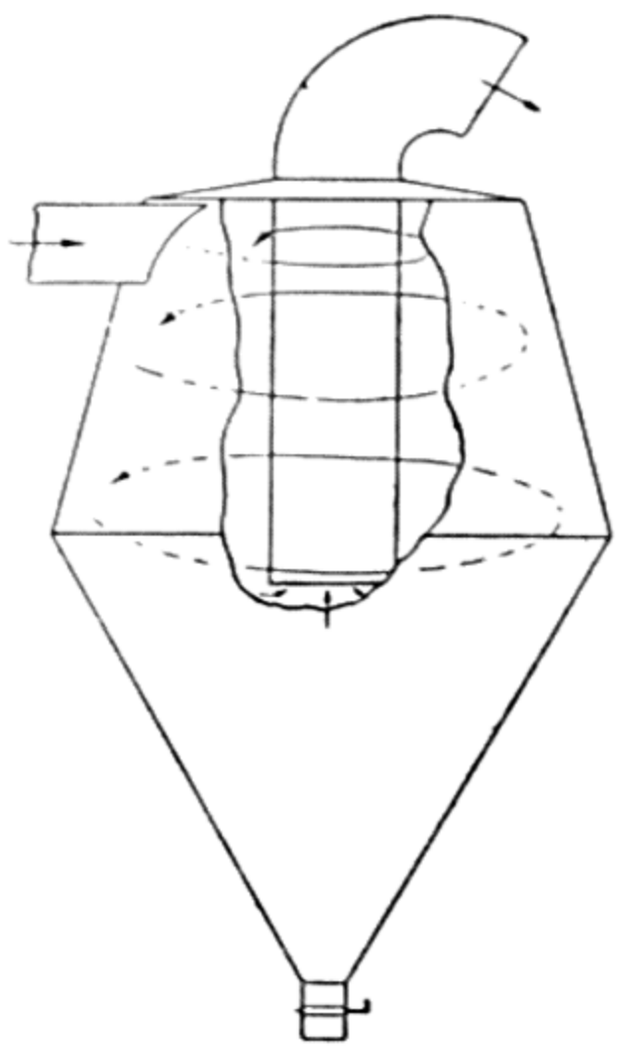


FIGURE 299.—A dust collector.

scale operation, and for special cases. The rotary dryer is a long cylinder lying on its side, resembling the portland cement furnace, but of light construction; warmed air is pulled through the cylinder, which travels in a direction opposite to that of the solid. The latter is fed in at one end, and moves to the opposite end gradually, by virtue of a slight inclination. A tunnel dryer consists of a long chamber through which small cars carrying the material are slowly or periodically moved one way while warm air travels the other way. The atmospheric drum drier consists of two hollow drums rotating toward each other, and internally heated by steam; buttermilk or

[3a] *See* Fig. 219.

[4] The shelf drier may be used at atmospheric pressure, and it may be circular and provided with rotating arms; for several shelves, the material may be moved from one shelf to another alternately, with central, then circumferential discharge; *compare* Chapter 4 under anhydrous bisulfite of soda.

tanning extract, for example, lies between the two drums; a thin film is carried down by each cylinder, and dries in a fraction of a revolution; a scraper detaches the powder. The speed is slow. The drums are furnished chromium plated, if desired; the evaporator may then be used for a number of products which would attack iron. The same evaporation may be performed at reduced pressure by placing the drum in a housing, providing a

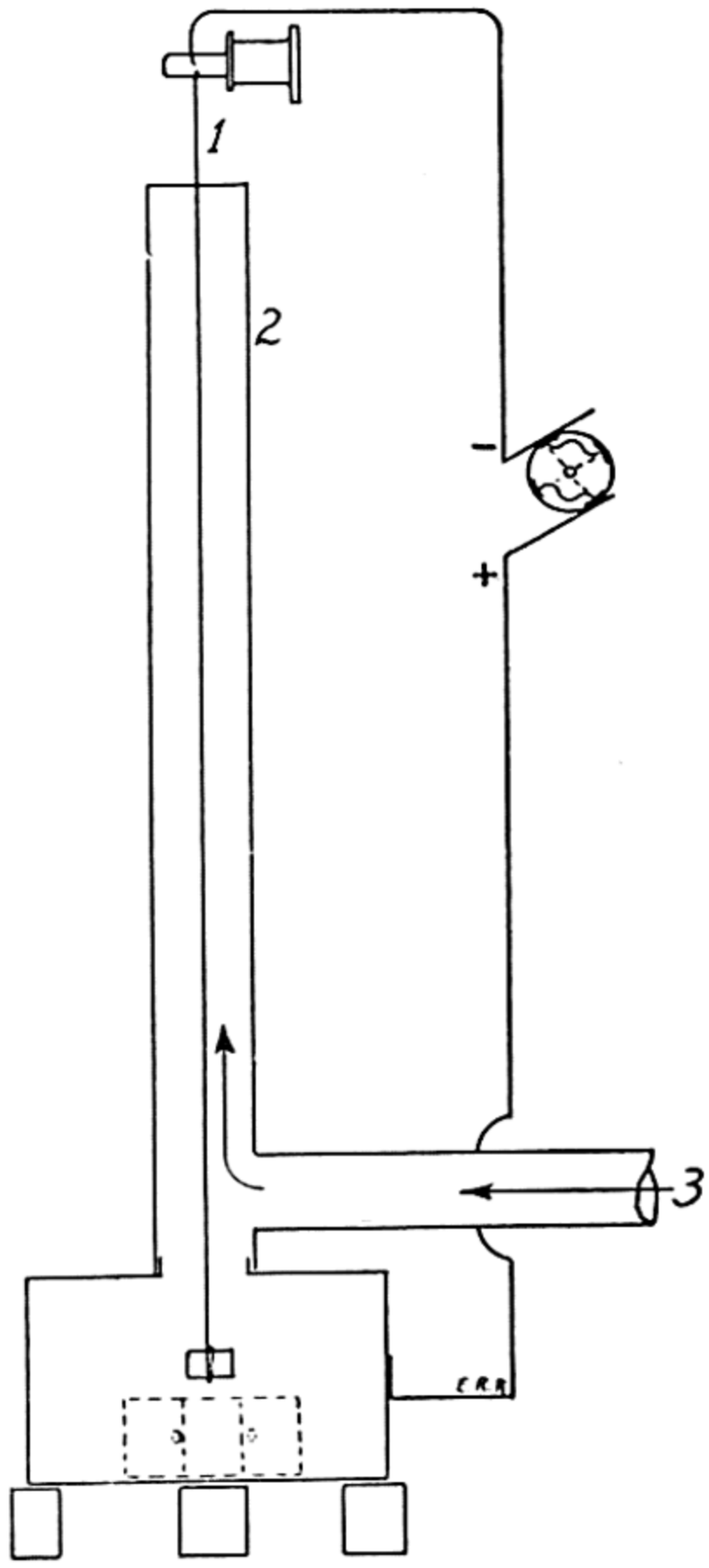


FIGURE 299a.—Principle of the Cottrell electrical precipitator. The high-tension direct current passes from insulated wire 1 through the air gap, to pipe 2; the dirty gas enters at 3; clean gas issues at 1. The dirt on the pipe drops into the box below on rapping.

suction pump, a small condenser, and a conveyor with store boxes inside the evacuated area; such vacuum drum evaporators are suitable for drying dyes and for milk evaporation (copperlined).

In the Flick catchall and entrainment separator, the vapors enter tangentially, so that a circular motion is set up. (*See* Figure 298.) The droplets or other suspended particles are thrown to the inner wall, and pass through its slits to the chamber between inner and outer wall, out of the path of the vapors or gas. The droplets collect and drain to a bottom discharge. The cleaned vapor leaves at the top of the separator. Such a separator is used between a single or multiple effect glycerin evaporator, for example, and the vacuum pump or ejector; any entrained liquid is recovered.

Dust Collectors. The gases from a blast furnace carry with them solid particles in the form of dust; the greater part of this dust may be recovered by passing the gases through a dust collector, such as shown in Figure 299.

The dust collector provides a space wider than the flue, in which therefore the velocity of the gases is reduced, and their carrying capacity correspondingly lessened, so that the dust deposits. Provision is made to feed the dusty gases along the walls on which the dust may deposit, and to draw the outgoing clean gas from the center, as far from the deposited or falling dust as possible. The dust collects in the cone and may be drawn out at intervals. The dust collector has no moving parts. There are several designs, but the principle is the same for all.

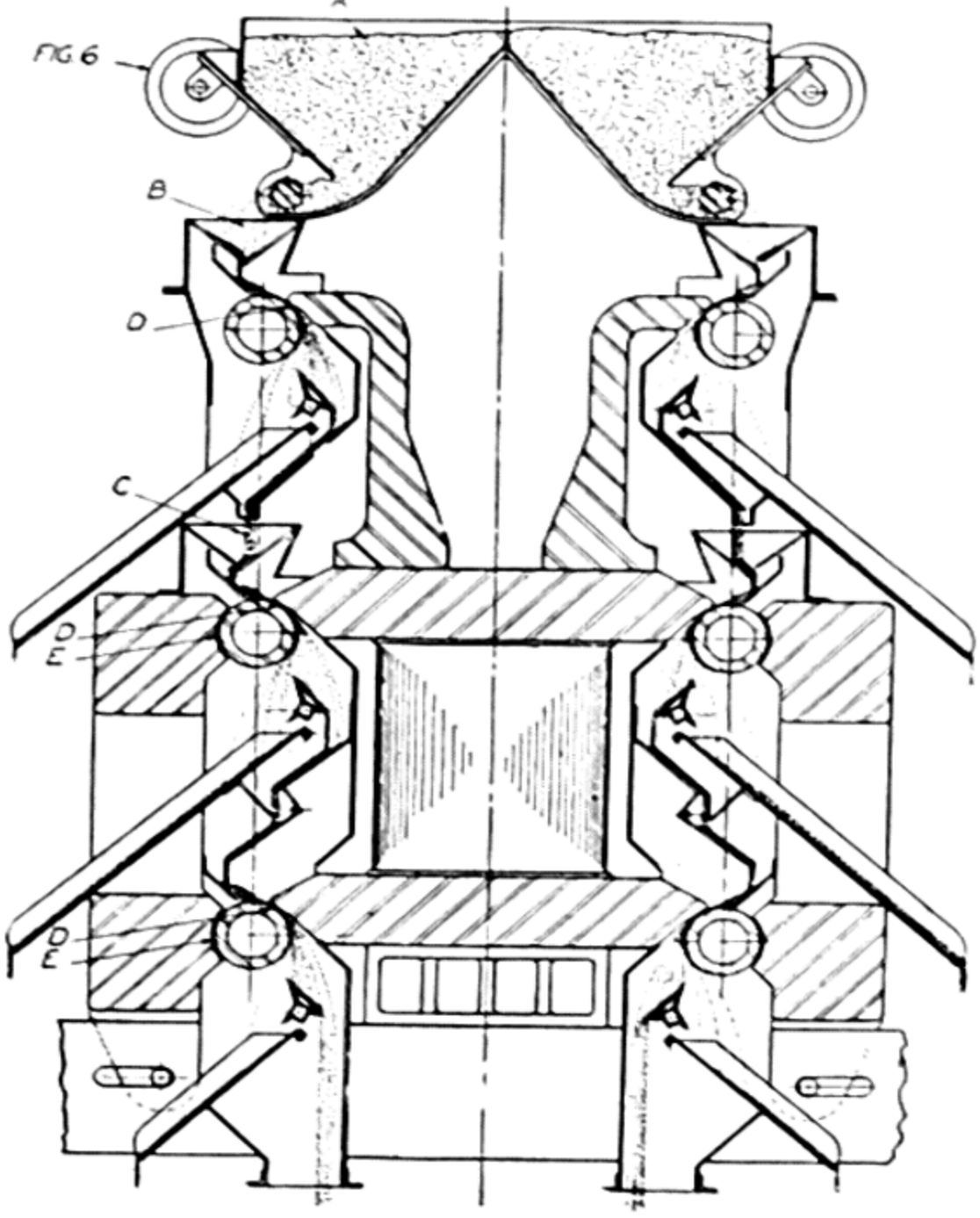


FIGURE 300.—Electromagnetic twin separator, type KT, with twin hoppers, twin feedrolls, and three high intensity induction rolls to each side. (Courtesy Stearns Magnetic Manufacturing Company, Milwaukee, Wisconsin.)

The Cottrell Precipitator. There are dusts, however, too fine to settle in the dust collector; furthermore, many gases carry fumes, finely divided droplets, or metallic particles just condensing from the vapor state, which no dust box will retain. Until some 20 years ago, there were no practical means to collect the particles in such fumes, but this may now be done by means of the Cottrell electrical precipitator. The gases are passed up a tube in which a copper (or lead-covered copper) wire is suspended; a high-tension direct current passes from the wire to the surrounding tube or pipe; particles of solids present in the gas are electrified by the silent discharge of the central wire, and are then attracted by the pipe, which has the opposite polarity. The gas issues from the top of the pipe free from dust. The effect on mists is the same. The solids deposited on the walls of the pipe are caused to drop off into the box beneath by rapping. Not only pipes, but rectangular spaces are suitable, with several central wires. A sketch of the single pipe used in preliminary testing is given in Figure 299A.

The voltage is used as high as possible, without causing a spark to pass; for the distance of 4 inches, such as that in an 8-inch pipe with central

wire, 75,000 volts may be used; for larger pipes, 100,000 volts; higher voltages than the latter are not the practice. High voltages for direct currents are produced in a round-about way; an alternating current is stepped up in an oil transformer (2 coils laid in oil), and mechanically rectified by means of a rotating cross driven by a synchronous motor. There is taken off the rectifying device an intermittent unidirectional, high-potential current, suitable for the precipitating pipe.

For treating large volumes of gases, enough pipes of the standard 15-foot length must be used to lower the velocity of the gas sufficiently to clean it; this velocity differs with the content of suspended solids or mist; an average would be 4 feet per second. A treater may consist of 60 or 100 pipes, which receive the dirty gas below, and deliver to a central flue the cleaned gas at the top; if one treater is not sufficient, a second one, or a third is installed. For very large volumes, rectangular passages are better suited.

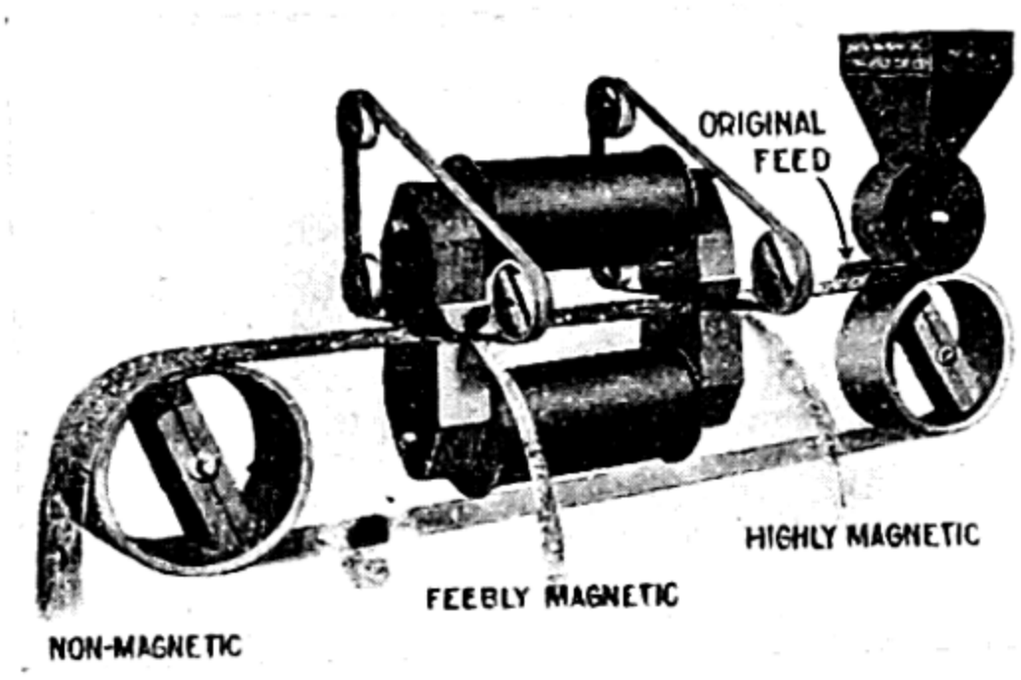


FIGURE 301.—The working principle of the Rowand-Wetherill cross belt separator. The magnetizable matter jumps up to the upper traveling belt, which carries it out of the field and drops it into a separate bin. (Courtesy Dings Magnetic Separator Company, Milwaukee.)

The electrical cleaning of fumes, fogs, and smokes, as it might also be called, has been applied to smelter gases, to sulfuric acid mists, to roasting furnaces, cement furnaces, and other cases. Undesirable gases such as sulfur dioxide are not retained by the treater; but cleaned of solids, the discharge is invisible, and causes less difficulty. In many cases, the material recovered has been salable and has paid for the installation; in other cases, the removal of a nuisance has prevented a shutdown by court order. The quantity of current used is not very great; for 250,000 cubic feet of gas per minute, at 100° to 200° C., the power consumption was 120 kilowatts.[5]

The Magnetic Pulley. The magnetic pulley (Dings [6]) is a device widely used to separate admixed old iron from non-magnetic materials, such as crushed bones, slaughter-house refuse, glass, and many others. The pulley is placed at the turn of a conveyor belt; the bones drop off at the turn, but the iron is carried a short distance along the under side of the belt, to a point just outside the magnetic field; there they drop off in a separate container. The pulley contains coil windings and iron; the coils are supplied with direct current through contact rings protected from dust and brushes (hollow shaft). The pulley is generally a driving pulley.

[5] "Problems in smoke, fume, and dust abatement," F. G. Cottrell, pp. 653-685, in the *Smithsonian Report* for 1913, with 37 illustrations and photographs. The power consumption figure is taken from p. 678.

[6] The Dings Magnetic Separator Co., Milwaukee, Wis. Similar equipment is made by the Stearns Magnetic Manufacturing Co., Milwaukee, Wis.

Magnetic separation of solids is performed by other devices, such as the Rowand-Wetherill cross belt separator, which in turn is being displaced by the high intensity induction rolls type machine, as for example the Stearns Type K separator, the Exolon, the Dings. The induction rolls type machines have greater capacity.

Mixers. A solid may be kept suspended in a liquid by means of rotating arms. In order to mix thick liquids, such as greases, the mixing arms are made to rotate in opposite directions; in general, the vessel used is

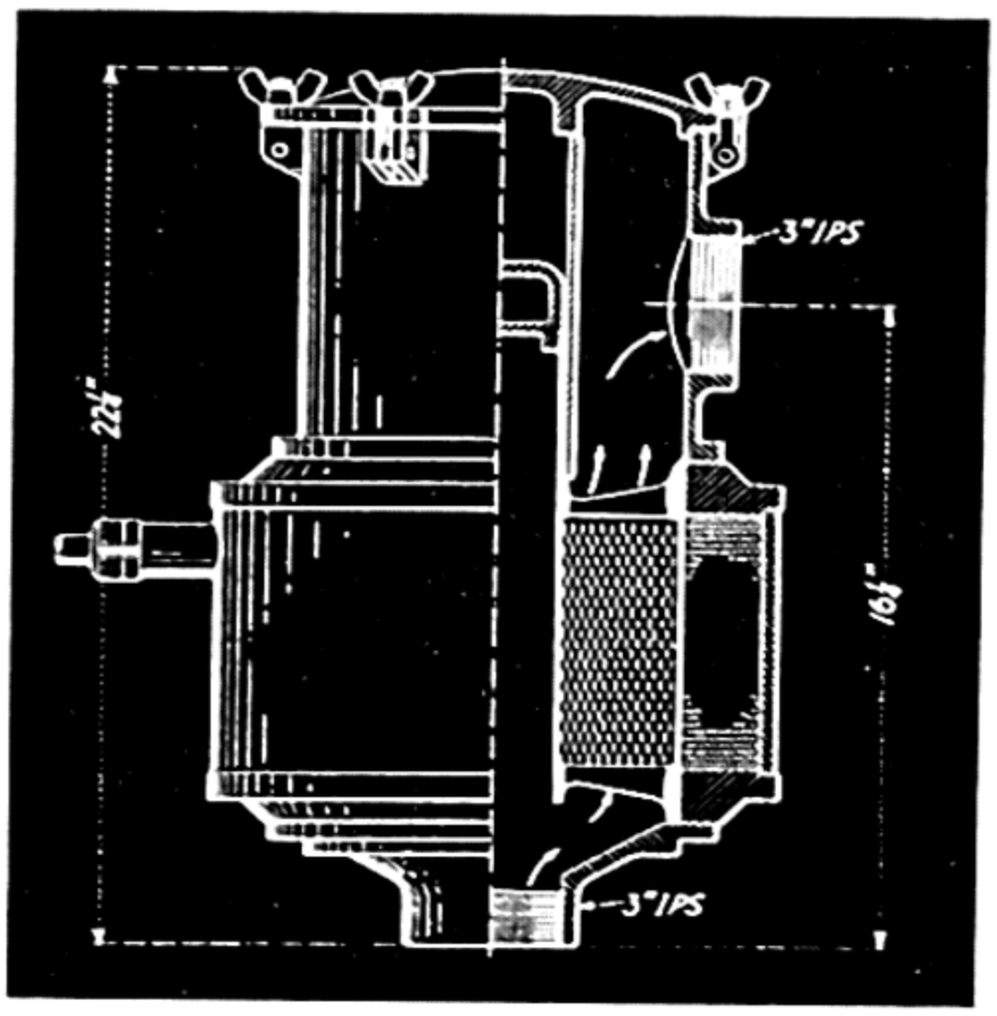


FIGURE 302.—An electro-magnetic separator for liquid; a partial cross sectional sketch of a Ferro Filter for liquids, of the pipe line type. As shown, the liquid travels upward through the screens which are magnetized by the coil surrounding them.

(Bulletin 15, S. G. Frantz Company, Inc., 161 Grand Street, N.Y.)

jacketed, so that heating may be furnished. It is essential to thorough and rapid mixing, as well as to rapid heating, that the walls be scraped. (*See* Figure 302.)

The Slurry Thickener. A slurry may be thickened by settling it, running off part of the water, and running off to the next operation a slurry richer in solids than the original one. The Dorr thickener is a settler with means for the continuous discharge of the thickened slurry, overflow of the clear water or thinner slurry, and constant feed of the original slurry. It consists of a tank with a bottom sloping toward the center, and 4 arms with plows, rotating slowly so as to drive the thick mud to a discharge pipe; the thin slurry overflows from a point near the side wall and near the top, while the original slurry enters at the center of the top layer. The Denver, Hardinge, and other thickeners are made in a number of designs, and with several working shelves if desired.

The Graver Continuous Clarifier is especially adapted to sugar juices and similar liquids. It has generally 5 shelves or compartments, and slow-moving arms with plows. The muddy liquor enters down the center; the clear liquor flows out at the upper part of each tray, at the circumference, while the thickened sludge flows down also at the circumference, but in a separate channel from the base of each shelf. There are numerous additional specialized settlers and thickeners on the market, each with its special merit.

The Dorr classifier will be found described in Chapter 49, under copper, and will serve as type for classifiers in general.

The Flaker, or the Chip Machine. The production of chemicals in chip form rather than in lump form has been possible by the employment of the chip machine. It consists of a hollow drum, cooled with water (or brine), over which a fused salt is distributed evenly by a small trough at the top and a larger dipping trough at the bottom; the drum turns at a slow rate, slow enough for the salt to congeal, and the thin solid layer formed is

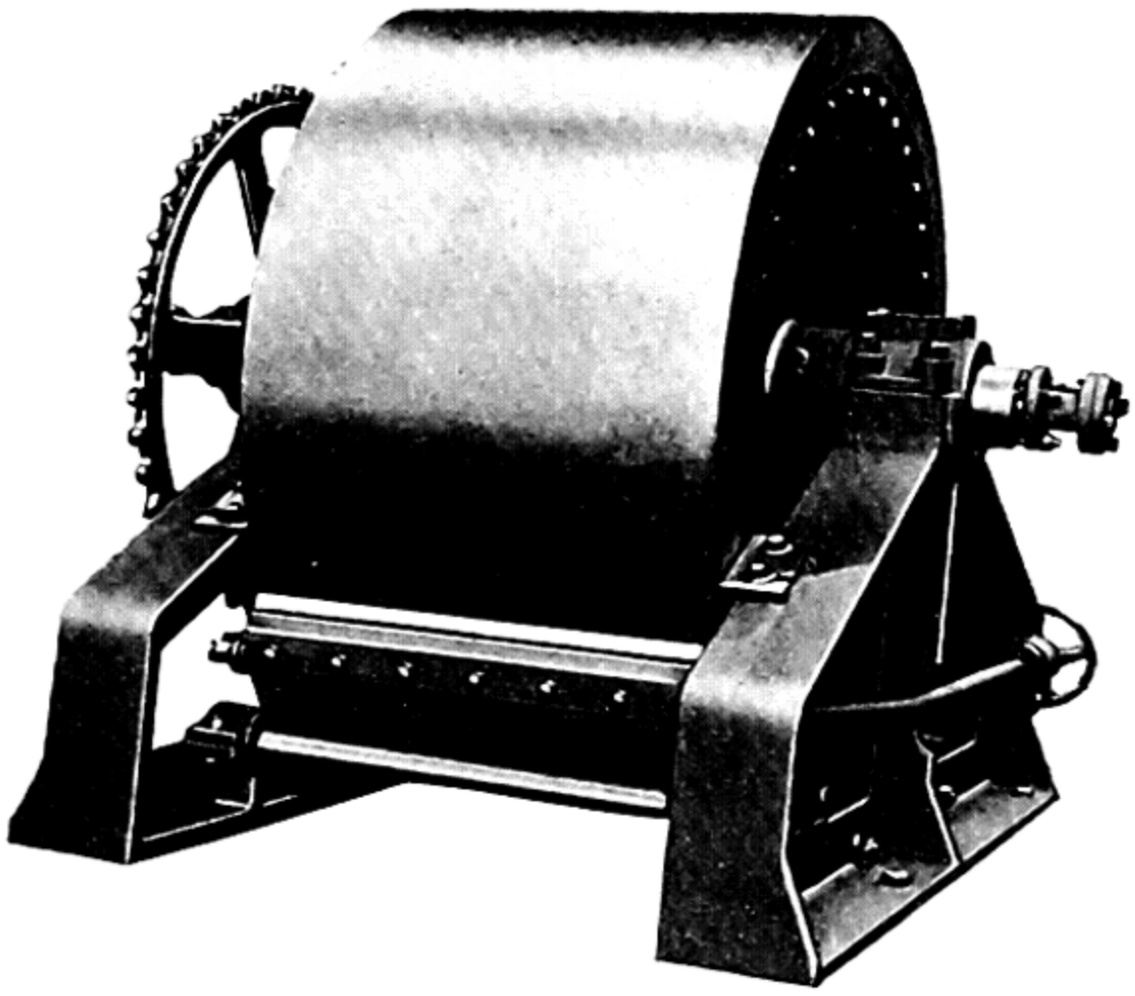


FIGURE 303.—A flaker, or chip machine. (Courtesy Buflovak Equipment Division, Blaw-Knox, Pittsburgh, Pa.)

scraped off by a stout knife running the length of the drum; as the layer falls to the movable bin below, it is broken into smaller pieces, easily shoveled into drums, easily dissolved by the consumer, readily weighed out to a given weight, and more uniform in quality. The cylinder may move smoothly, turned by a gear wheel, or it may move by jerks, by means of a ratchet. The thickness of the chips or flakes is controlled by the rate of feed. Occasionally one difficulty is that the layer sticks to the roll so well that the knife does not peel it off readily; there are various remedies, of which one is to place some paraffin in the lower trough. A lower temperature within the drum may also prevent sticking.

OTHER PATENTS

U. S. Patent 2,040,431, fractionating apparatus, with 2 figures; 1,889,349, a magnetic separator especially adapted for use in connection with coal crushers; 1,885,717, a magnetic separator especially adapted for separating gold and other magnetic material from sand, etc.; 1,836,252, a magnetic separator; 1,857,884, precipitator, whereby salt or other material, the solubility of which vary with temperature, is precipitated by changing the temperature by means of heat transfer; 1,884,726, an evaporator comprising an upright dome especially adapted for evaporating milk (Kermer); 1,885,402, apparatus for continuous evaporating or distillation employing a vacuum and only a short heating period; 1,907,197, continuously precipitating dust collector; 1,821,842, a dust collector for collecting the dust from grinding, sanding and polishing machines by passing through a chamber containing baffle plates; 1,844,591, dust collector for

cement mills; 1,906,534, crystallizing apparatus consisting of a high vertical shell, an agitator within the shell and a means of removing the crystal from the bottom of the shell; 1,860,741, a crystallizer in which a supersaturated liquid is passed upward through a suspension of crystals of substance to be precipitated; 1,810,217, a continuous crystallizer using a helical ribbon conveyor to prevent adherence of crystals to cooling surface as well as carry the crystal and liquor through the crystallizer; 1,884,727, rotary drier in which material to be dried is deposited in a thin film on the periphery of an internally heated drum and then scraped off the drum (Kermer); 1,867,465, a steam drier and means for extracting grit and dust from air; 1,882,405, a rotating drum drier especially suitable for drying silica.

Reading References

"The evaporator experiment station at the University of Michigan," W. L. Badger and P. W. Shephard, *Am. Inst. Chem. Eng.*, 13, I, 77 (1920).

"The electrical precipitation of suspended particles," F. G. Cottrell, *Ind. Eng. Chem.*, 3, 542 (1911), with 30 illustrations.

"Centrifugal dryers and separators," Eustace A. Alliott, London, Ernest Benn, Ltd., 1926.

"Modern drying machinery," H. B. Cronshaw, London, Ernest Benn, Ltd., 1926.

"Evaporation," Alfred L. Webre, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1926.

"Tools of the chemical engineer, VI—Centrifugal machines," D. H. Killeffer, *Ind. Eng. Chem.*, 19, 287 (1927).

"Equipment for nitration and sulfonation," R. Norris Shreve, *Ind. Eng. Chem.*, 24, 1344 (1932).

"Drying by means of air and steam," E. Hausbrand, translated by A. C. Wright, New York, D. Van Nostrand Co., 1924.

"Evaporating, condensing and cooling apparatus," E. Hausbrand, translated by A. C. Wright, New York, D. Van Nostrand Co., 2d. ed., 1933.

"Some experiences with Cottrell precipitators in the purification of burner gases," J. J. Healy, Jr., *Am. Inst. Chem. Eng.*, 24, 37 (1930).

"Distillation columns: Distillation advances in column design," D. B. Keyes, *Chem. Met. Eng.*, 18, 226 (1931).

"The efficiency and design of rectifying columns for binary mixtures," W. K. Lewis, *Ind. Eng. Chem.*, 14, 492-7 (1922). In this article, basic equations of general applicability have been devised, which may be used in the determination of the best practical overflow, of the number of plates required, and of the point of introduction of the feed.

"Symposium on distillation," *Ind. Eng. Chem.*, 14, 476 (1922).

"Graphical design of fractionating columns," W. L. McCabe and E. W. Thiele, *Ind. Eng. Chem.*, 17, 605 (1925).

"Principles and practice of industrial distillation," E. Hausbrand, translated by E. H. Tripp, New York, John Wiley & Sons, Inc., 1926.

"Plate efficiency and entrainment in distillation," F. H. Rhodes and Preston G. Slachman, *Ind. Eng. Chem.*, 29, 51 (1937).

"Studies in the fractional distillation of crude petroleum," M. B. Cooke and H. P. Rue, *Bur. Mines Tech. Paper* No. 431 (1928).

"Some experiences with Cottrell precipitators in the purification of burner-gases," J. J. Healy, Jr., *Trans. Am. Inst. Chem. Eng.*, 24, 37 (1930). This article describes a "hot Cottrell" operating on the dust in burner-gas, and in addition a "cold Cottrell" or mist collector.

"Dependence of reaction velocity upon surface and agitation," A. W. Hixson and J. H. Crowell, *Ind. Eng. Chem.*, 23, 923 (1931).

"Effects of scrapers on heating, cooling, and mixing," F. E. Huggins, *Ind. Eng. Chem.*, 23, 749 (1931).

"The continuous centrifugal and some of its applications," E. M. James, *Trans. Am. Inst. Chem. Eng.*, 26, 224 (1931).

"Spray drying and the drying of dairy products," J. E. Nyrop, *J. Soc. Chem. Ind.*, 48, 136T (1929).

"Graphical rectifying column calculations," T. Baker and Jay S. Stockhardt, *Ind. Eng. Chem.*, 22, 376 (1930).

"Some fundamental principles of drying," E. A. Fischer, *J. Soc. Chem. Ind.*, 54, 343T (1935).

"Mechanical crystallisation," Hugh Griffiths, *J. Soc. Chem. Ind.*, 44, 7T (1925).

"Thickening calcium carbonate slurries," E. W. Comings, *Ind. Eng. Chem.*, 32, 663 (1940).

"Filter type dust collectors," L. J. Weischhaus, *Chem. Eng.*, 54, 113, Aug. 1947.

"Pebble heater, new heat transfer unit for industry," C. L. Norton, Jr., *Chem. Met. Eng.*, 53, 116 (1946).

Frequently the success of a new process depends not upon the correctness of the chemical calculations, but on the proper choice of the mechanical device which automatically brings the raw materials to the reaction chamber, or on the device which, again automatically, takes the product away; for an industrial operation must be profitable or it cannot live. It will be apparent that the importance of an acquaintance with the ordinary mechanical devices which an industrial chemist needs cannot be overestimated.

Chapter 44

Appliances Used by the Chemical Engineer
IV. Crushers, Disintegrators, Pulverizers

The handling of liquids and gases is a comparatively simple matter: applying pressure at one part brings a quick response from every other; they are of uniform texture; where one part will pass, all the others will. Not so with solids; pressure at one end of a long pipe filled with a solid of assorted sizes would only jam it fast, except for an impalpable powder. Solids must be carried all the way from one spot to another in a wheelbarrow, or in a succession of little barrows or buckets which deliver their load and return to the starting point for another. By making the chain carrying them an endless one and running it over two sprocket wheels, upward and with the load, on one side, and down, empty, on the other, we achieve the automatic elevation of a solid in its simplest form, that of the *bucket elevator;* traveling vertically, it lifts coarse solids to an elevated delivery point. The chain and buckets are enclosed in a steel housing which prevents loss and dust nuisance; the housing has a feed hopper at the bottom, also called the boot; the buckets pass through the solid; a delivery spout is also part of the housing, at the top. The operation is indicated further in Figure 304. The chain is usually belt-driven; the driving pulley is part of the upper sprocket shaft; the lower sprocket is merely an idler. The buckets are of various sizes, rarely over 4 inches by 8 inches; the travel is slow, about one foot a second, and the capacity rather small.

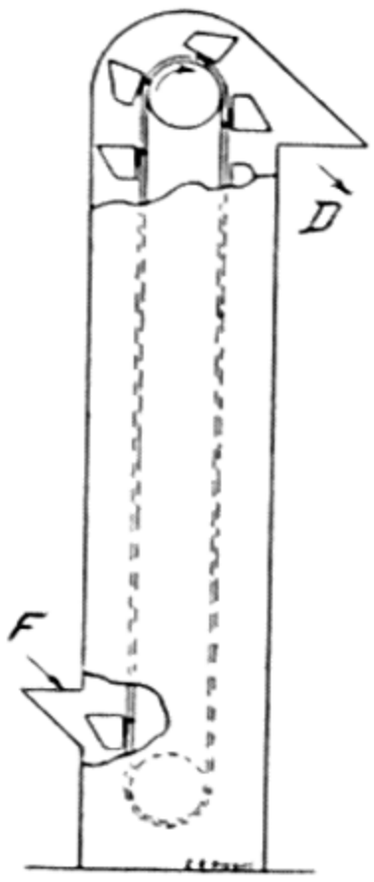


FIGURE 304.—The bucket elevator. *F*, feed; *D*, discharge.

When a large capacity is needed, an elevator on which heavy barrows may be loaded is used, or a skip hoist.

In the form most commonly used in chemical operations, the buckets in the bucket elevator are at some distance from each other; there are also in use bucket elevators in which the buckets shoulder each other, and cover the chain completely. The other extreme is a form which has only two buckets, of large size, which are so disposed that one descends as the other ascends; both reach the end of their respective trips simultaneously; this type is called the *skip hoist*. It does not include an endless chain; the bucket is really a small car traveling on inclined rails, which is pulled up the incline by a drum-wound cable. The skip hoist has no casing. It is used, for instance, for lifting ore, coke, and limestone to the top of an iron blast furnace.

The Conveyor. In order to move solids from one point to another on the same level, conveyors are used; among the various types may be mentioned the belt conveyor, made of leather or reinforced rubber; the screw conveyor, usually of metal, and the pneumatic conveyor.

The belt conveyor is well adapted to long trips, that is, 100 feet or more [1]; if the material must travel along one level, then up an incline to an elevated level, and still another distance along the upper level, a belt conveyor in a single piece will give the required service.

The belt conveyor is pulley-driven, and rests on small rollers or idlers; on the up-travel the loaded belt passes over auxiliary idlers placed under its two edges slant-wise so that the edges are turned up slightly; the solids cannot roll off. The speed is not high, perhaps one foot in two seconds, but the capacity may be made high by using a wide belt.

By causing one belt to dump its load on a second one traveling at right angles to it, the material carried is made to turn a corner.

For moving solids along the level, screw conveyors are used, if the distance is short. They consist essentially of a wide sheet-metal screw fitted to a gutter with rounded bottom; the screw shaft is driven by a pulley; as it turns it pushes the solids along the gutter, until they reach an opening which delivers them to a bin, for instance. Vertical screw conveyors are also in general use for special services. Two remarkable conveyors are the Redler "en masse" conveyor, and the Johns split rubber tube conveyor.

A pneumatic conveyor is used for elevating solids, for example for conveying loose soda ash from a box car to a steel storage tank placed on the roof to permit feeding to various dissolvers by gravity. The installation comprises a suction pump protected by a dust collector, an air-tight steel bin, and the suction line, partly steel, and partly of rubber, ending in a strainer which is introduced in the car. The fine powder mixed with air travels up the pipe until it reaches the bin when it drops, because the velocity of the air drawn in is reduced. The air travels further to the dust collector, then to the pump.

The Fuller-Kinyon pump, mentioned elsewhere, is a pneumatic conveyor.

[1] A belt conveyor four miles long is described in *Chem. Met. Eng.*, 32, 159 (1925).

Poidometer. The poidometer is a device for the continuous weighing of a loaded moving belt, with regulation of the load. The device is placed at the base of a bin, with a small hopper of its own. The belt rests on a pulley which actuates a beam with weights. The beam in turn actuates the gate from the hopper; if too much material is fed, the pulley is depressed, the beam rises, and the gate drops. The graduation on the scale is in pounds per running foot of belt; a separate device records the running feet of belt, so that total poundage is automatically recorded, and with proper setting, assured. The accuracy is within 1 per cent. The capacity varies with the size of the poidometer and with the bulk weight of the material; it may be 1 pound per minute or 10,000 pounds per minute.

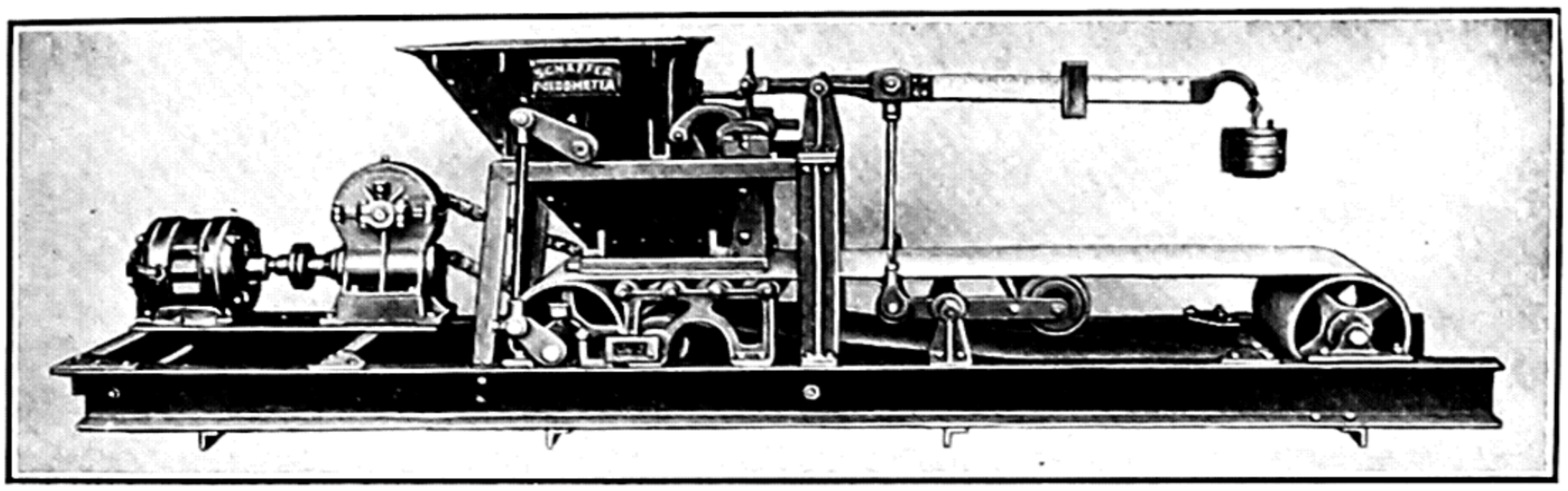


FIGURE 305.—The essential parts of a poidometer. (Courtesy of Schaffer Poidometer Co., Pittsburgh, Pa.)

CRUSHING, DISINTEGRATING, AND PULVERIZING

A distinction is made between crushing, disintegrating, and pulverizing; the lines cannot be drawn with accuracy, for usage differs; for the sake of clearness the distinction will be assumed to be definite. In general terms, crushing means the reduction of large pieces, such as a man can just carry, to egg and nut sizes; the reduction of egg and nut sizes to a coarse powder is termed disintegrating, also grinding; finally, the reduction of the coarse powder to a powder so fine that the separate granules cannot be felt between the fingers is termed pulverizing; these latter fine powders are aptly termed impalpable.

The sizes resulting from these operations are never uniform; a mixture of sizes is obtained which must be graded by sieving or screening; the definition of sizes is then made in terms of the percentage which will pass through a given screen, the remainder being termed "on the screen." Sieves and screens are described by the number of holes or meshes to the lineal inch, if small, or by the dimension of the hole in inches if large; the holes are regular, either circular or square, hence giving the number to the lineal inch defines them. The circular holes are made by punching a steel plate; the square holes are made by weaving iron or other wire, and are called meshes.

The distinction above may then be repeated in terms of meshes. Large lumps are "crushed" to pass through a three-inch mesh; "disintegrating'

means reducing the size so that 90 per cent, or so, will pass a ten-mesh screen, that is, through a screen having ten meshes to the inch; "pulverizing" means reducing so that 90 per cent, or so, will pass a 100-mesh screen or better, that is, will pass through a screen having 100 meshes or more to the inch.

Crushing is done in gyratory crushers, jaw crushers, and rolls; disintegrating is done in pot crushers, rotary-hammermills, squirrel-cage disintegrators, and stamp mills; pulverizing is done in buhrstone mills, suction mills, ring-roll mills, pebble mills, and edge runners. There are many

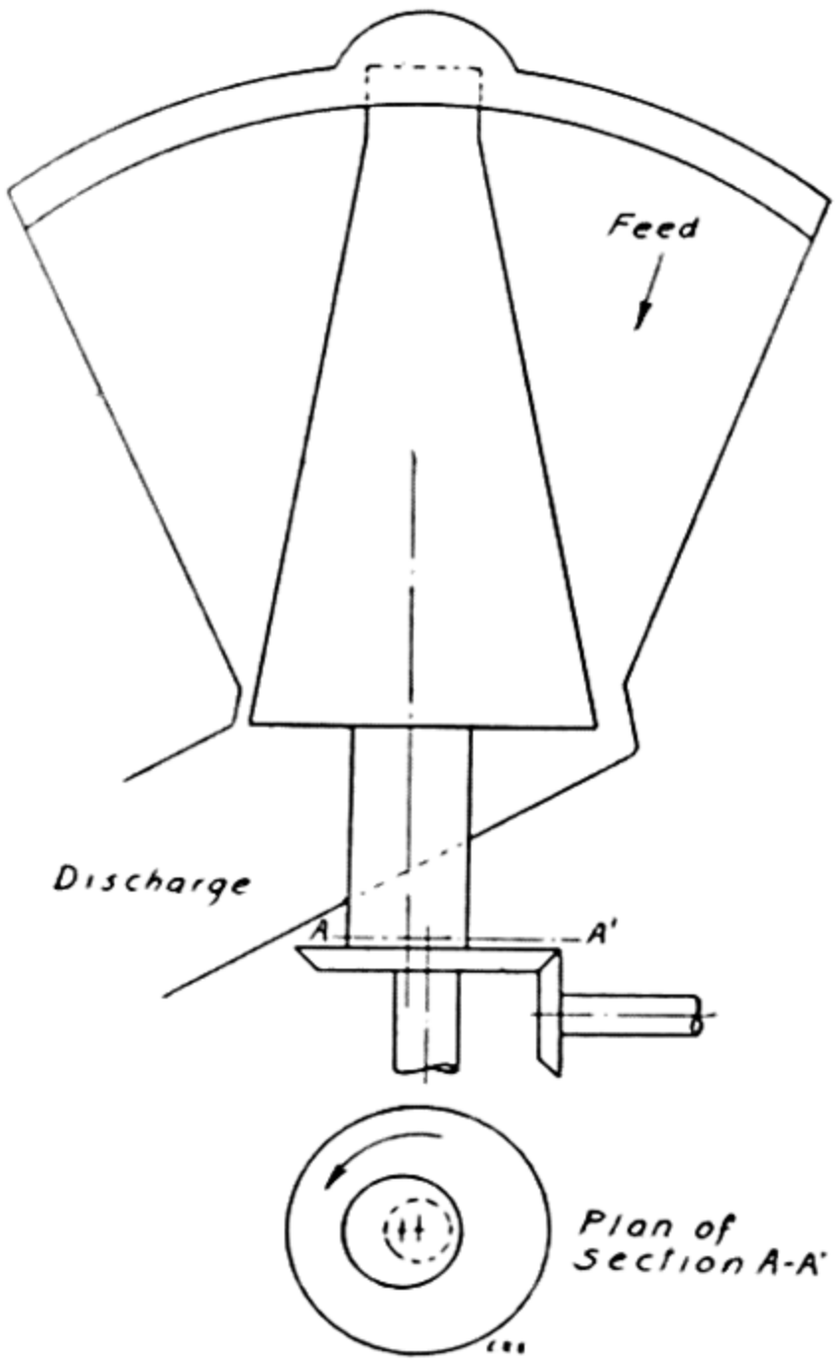


FIGURE 306.—The gyratory crusher, a pot crusher with the gyrating element set eccentric to the pot.

other special devices in addition to the ones listed which are used for reducing the size of a solid. Modifications of those given fit them for two classes, but in general the devices are listed as they would come to the mind of a plant man when the three classes of service are mentioned.

The Gyratory Crusher. The gyratory crusher is a pot crusher in which the gyrating element is set slightly eccentric to the pot in which it works. Figure 306 indicates its construction. The rock slides down in the wide opening made at the half-turn when the space is widened; at the next half-turn the space is too narrow to accommodate the piece and it is crushed. The gyrating element is smooth, or grooved. In size the gyratories are built with gyrating elements from 3 inches in diameter to 72 inches; the large sizes are the best known. The crusher with the 72-inch crushing head is 45 feet over all, makes 175 r.p.m., and requires 300 to 500 horsepower. It is usually belt-driven; when an unbreakable object finds its way into the pot accidentally, the belt slips and no damage is done to the gears. The large sizes are well adapted to reduce the large lumps brought from a mine or from the quarry, such as gypsum and cement rock, to egg size.

The Jaw Crusher. The jaw crusher has a back-and-forth motion; here too the lump slides down as the space widens and at the next forward stroke is crushed to smaller sizes. It is a powerful crusher; its crushing plates vary in size from 2 by 6 inches to 12 by 26 inches and over. It is most commonly used in medium sizes. To prevent injury when an un-

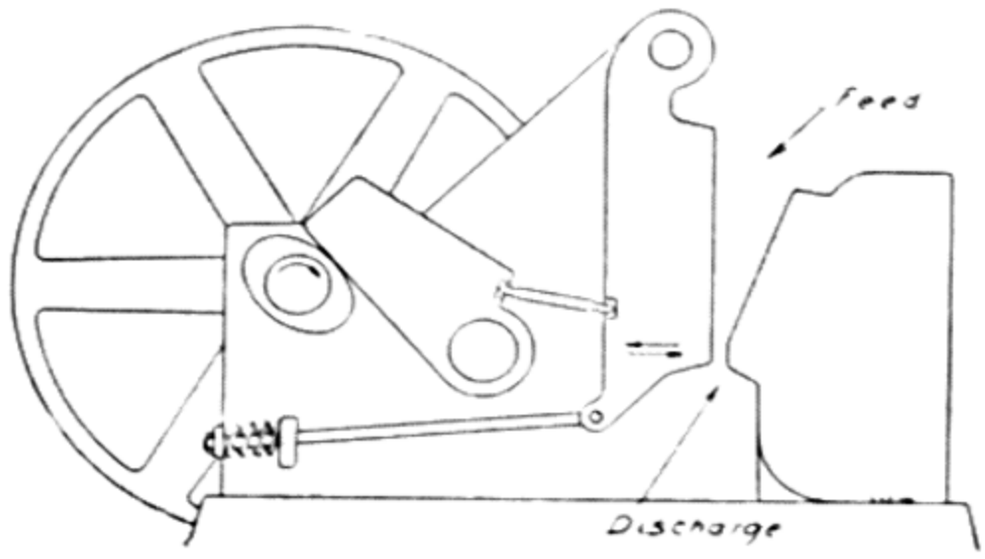


FIGURE 307.—The jaw crusher.

breakable object finds its way between the jaws, a weak point is provided by connecting the moving jaw to the driving shoulder by a slender rod, which breaks, and which is quickly replaced after the foreign object has been removed. The translation of rotary motion to the back-and-forth motion is by means of an oval, mounted on the pulley shaft, as indicated in Figure 307.

The crusher with plates 12 by 26 inches makes 140 complete strokes, that is, back-and-forward trips, per minute; it requires 25 horsepower; crushing to pass 1½-inch mesh its capacity is 12 to 15 tons per hour, half a carload; crushing to pass 2-inch mesh, 20 to 30 tons per hour. The greater capacity of the coarser size is due to the wider spacing between the jaws, which permits more material to pass through.

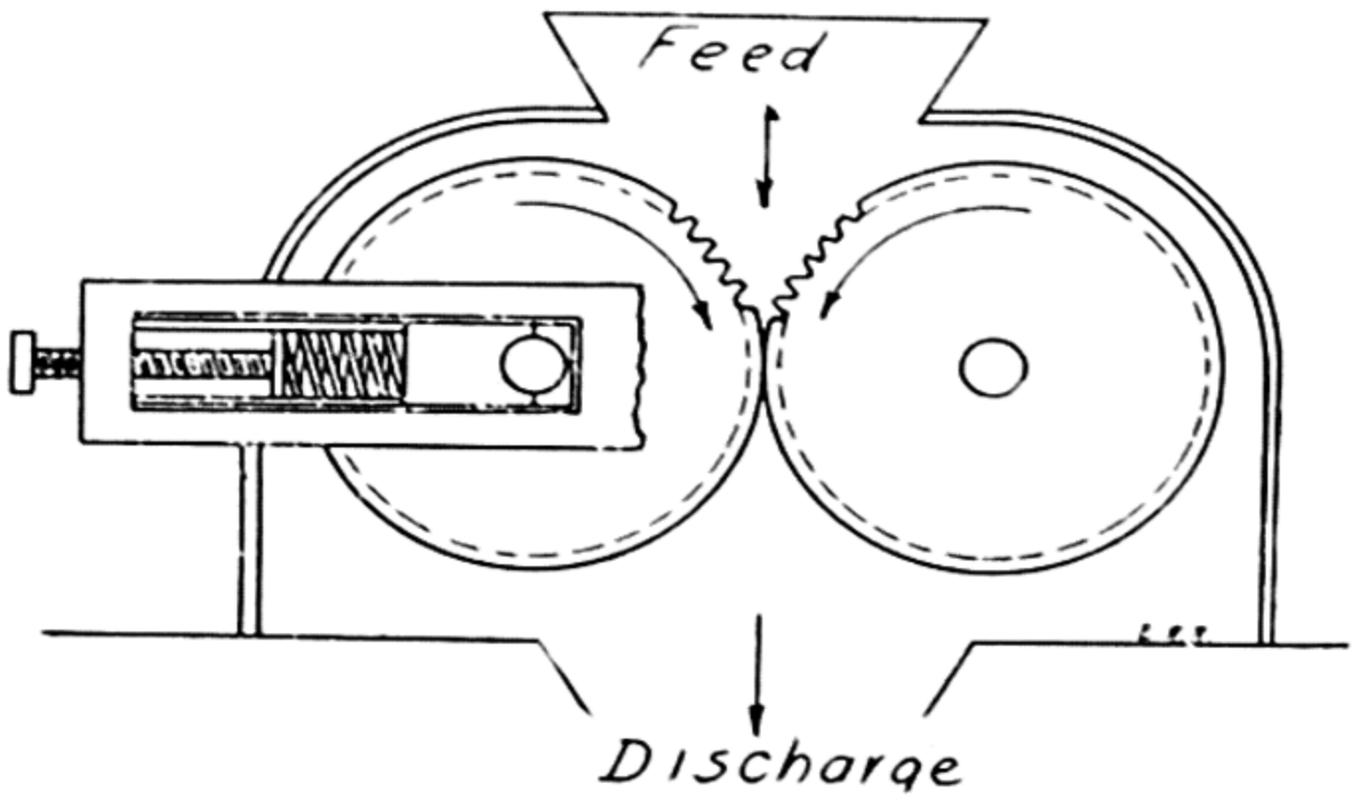


FIGURE 308.—Crushing rolls.

The Rolls. Rolls are used in many sizes, usually double, the rolls rotating toward each other; their surfaces are corrugated or spiked. (Figure 308.) They are well adapted to materials which crush easily, such as coal, bones, or coke. Provision against destruction is made by mounting one of the two rolls in journal boxes which can be forced back against stiff springs in case an unbreakable object is introduced; through the temporarily

widened space, it drops through, and the normal spacing is made again. Perhaps it should be added that the shafts of the rolls are horizontal, the material is fed in from above, and passes through by gravity. The operation will be clear from the drawing. Instead of two rolls, a single roll working against a fixed plate may be used. The capacity of a roll crusher is high.

Rotary Hammermills. A comparatively new type of disintegrator is the rotary hammermill, of which there are many variations. The mill shown in Figure 309 is the Jeffrey; it is one of the three best-known examples, the other two are the Williams and the Gardner.

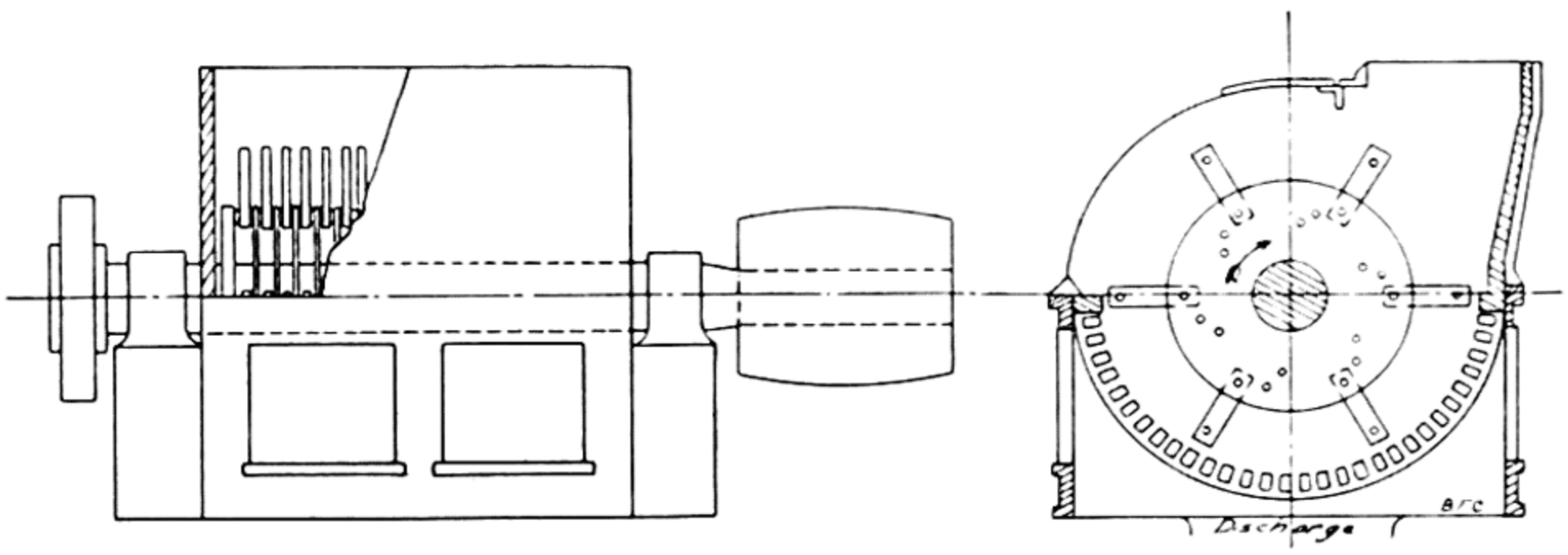


FIGURE 309.—The Jeffrey crusher, illustrating the rotary hammermill type of disintegrating device.

The hammers are steel bars free to pivot on a pin inserted in a central disk integral with the horizontal shaft. As the disk rotates, the hammer is whipped with great force against the incoming lumps; these are caught between the stationary breakers plate, of manganese steel, and the whirling hammers. The solid is reduced to small sizes which pass down through the semi-circular screen forming the lower part of the casing. The speed of the shaft is high, between 600 and 2500 r.p.m., so that to describe the action as cyclonic is rather apt. A long list of materials may be treated in these mills, including asphalt, nitre cake, gypsum, lime, bone for case-hardening of steel, cottonseed press cake, cinders, clay, and clam shells.

No provision is necessary against unbreakable objects of small size; the hammers can bend back and pass over them; the decreased discharge will reveal that there is an obstruction.

The hammers wear fast; in order to get as much use out of them as possible several holes are provided in the disk, so that they may be moved forward toward the edge as they become shorter; at the stage shown in the figure, they are quite short, and have been moved twice.

The shape of the hammer varies with the use intended; it may be a straight bar, a twisted one, blunt or sharp; it may be a yoke instead of a bar, of manganese steel, free to pivot like the plain bar.

The *pot crusher* is one of the older types of disintegrating device. Its construction is the same as that of the gyratory except that its rotating element is centered.

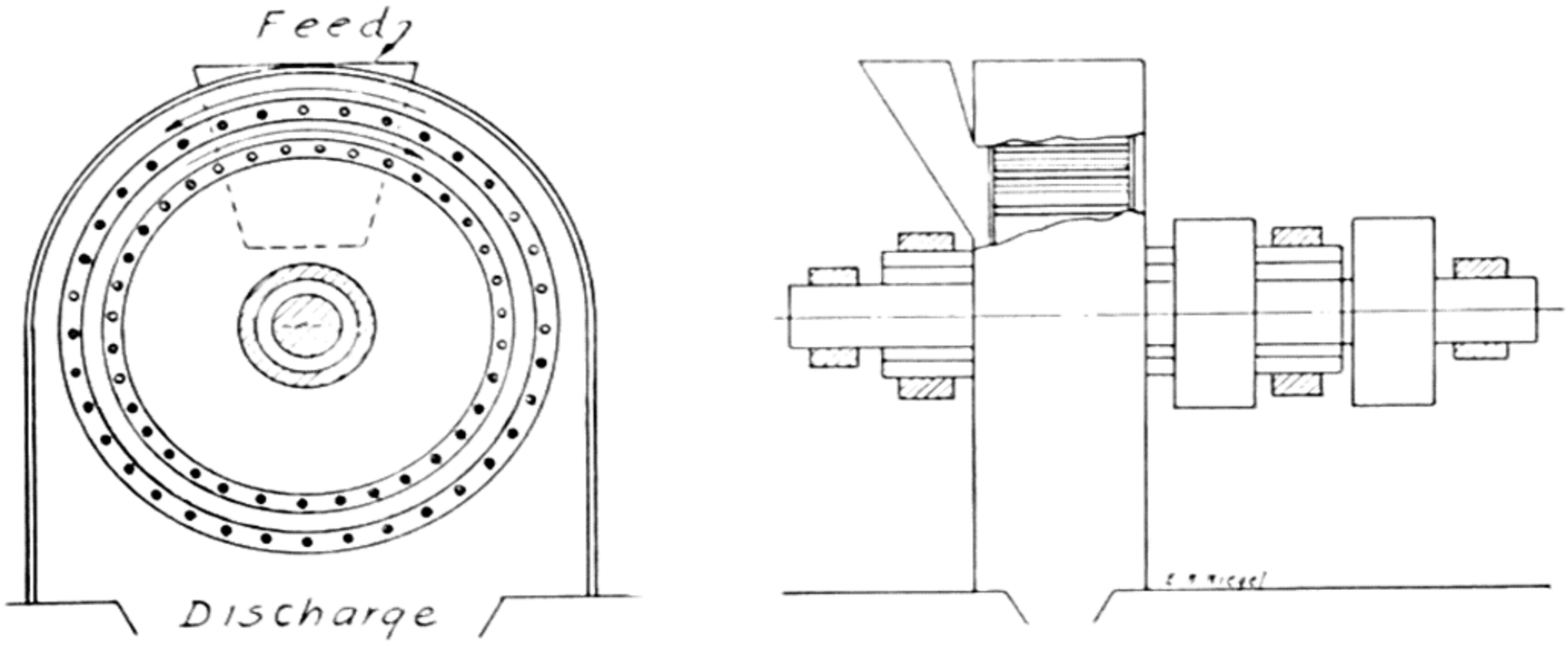
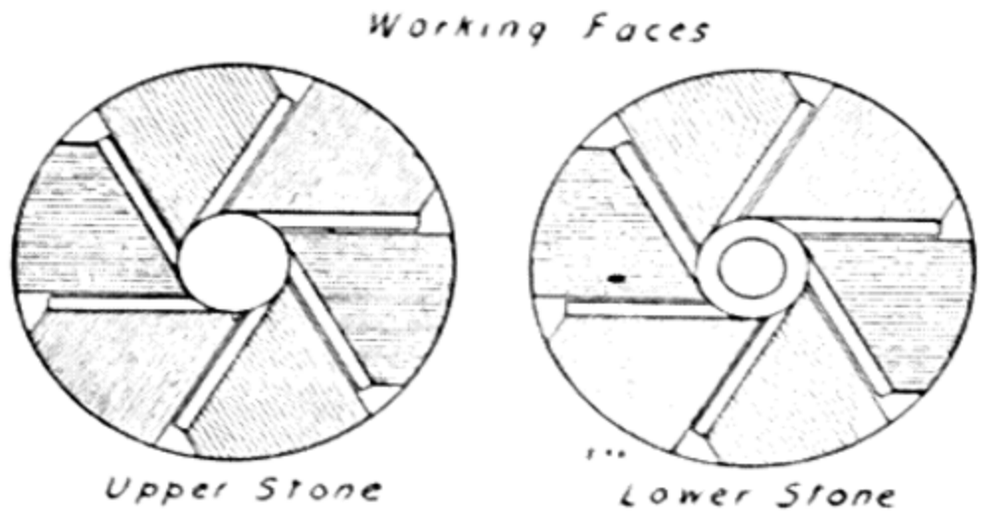


FIGURE 310.—The squirrel-cage disintegrator.

In the *squirrel-cage disintegrator,* two circular cages of steel bars mounted on steel rims, concentric, rotate in opposite directions. The material to be disintegrated is fed in the center, and must pass between the two cages. The squirrel-cage disintegrator is used to prepare coarse powders, for instance, ground nitre cake sold in cans for household uses; the powder must not be too fine, and no uniformity of size is sought.

The *buhrstone mill* is one of the oldest pulverizing devices. Formerly it was used by the millers for preparing flour; in the large mills of the Middle West it has been displaced by special corrugated rolls which tend to elongate the wheat kernel rather than pulverize it. In the chemical industries it is rarely used.

FIGURE 311.—The buhrstone mill.



The Suction Mill. In the suction mill, the material is ground between rotating horizontal wheels of small diameter, thrown by centrifugal force against the inner face of a larger, stationary ring; the material must be so fine that a current of air drawn through the mill can sweep it along as a fine dust; until that fineness is reached, the material remains subjected to the action of the mill proper.

The best-known mill of this type is the Raymond. It consists of the mill proper, a dust collector, and an exhauster. In the mill four smaller wheels are suspended from the arms of the vertical shaft in such a way that they are swinging freely; the centrifugal force presses them against the grinding ring, as shown in Figure 312; here the grinding, or better, pulverizing, takes place. The speed of the shaft (vertical) is about 100 r.p.m. Air is drawn in through the feed box or through the floor of the mill; the

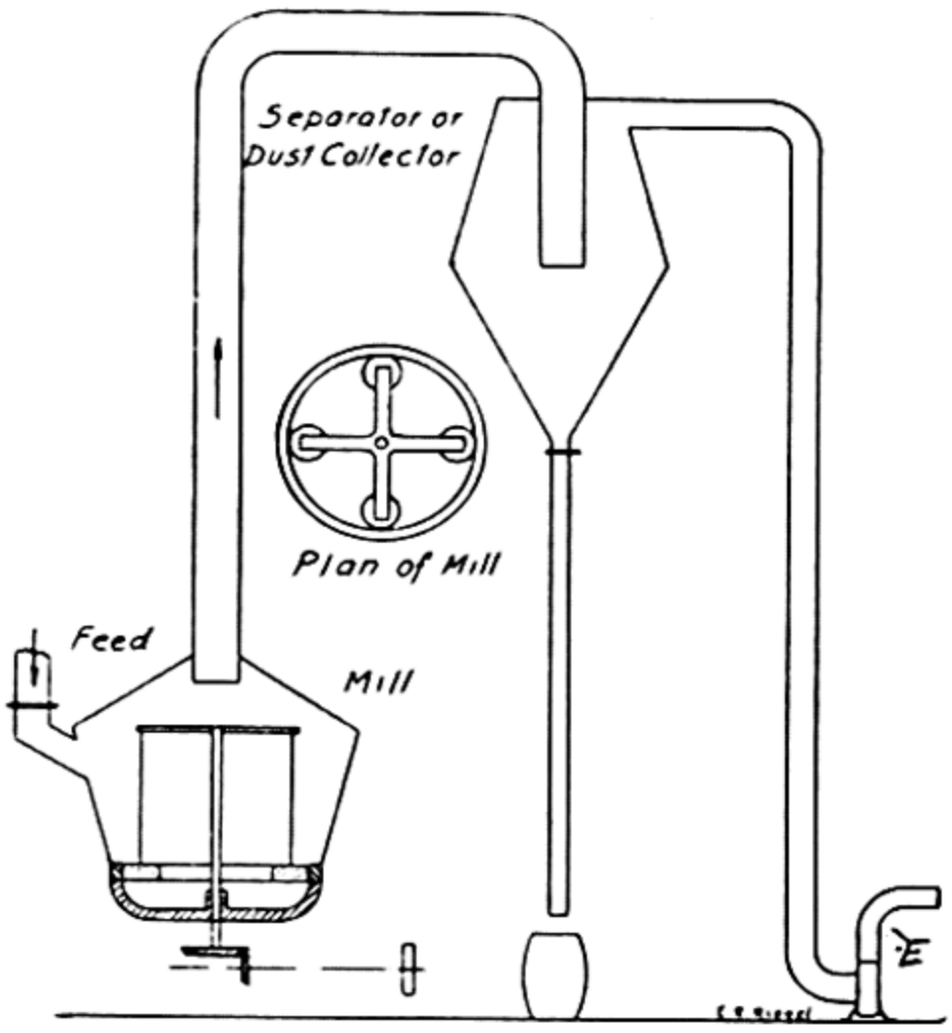


FIGURE 312.—The Raymond mill, illustrating the suction type of pulverizers. *E*, exhauster.

fine powder, really dust, is carried up the pipe into the dust collector or separator; here the dust is deposited, and the air, now free from solids, passes to the exhauster. It is rare that the discharge from the exhauster is free from the dust, and that is one reason why this air is frequently led into the mill again, entering below the stationary ring.

The Pebble Mill. The pebble mill in its simplest form consists of a porcelain jar containing a few pebbles; by placing it on the arm of a wheel it may be swung in a circle. As the pebbles glide, the pulverizing process takes place.

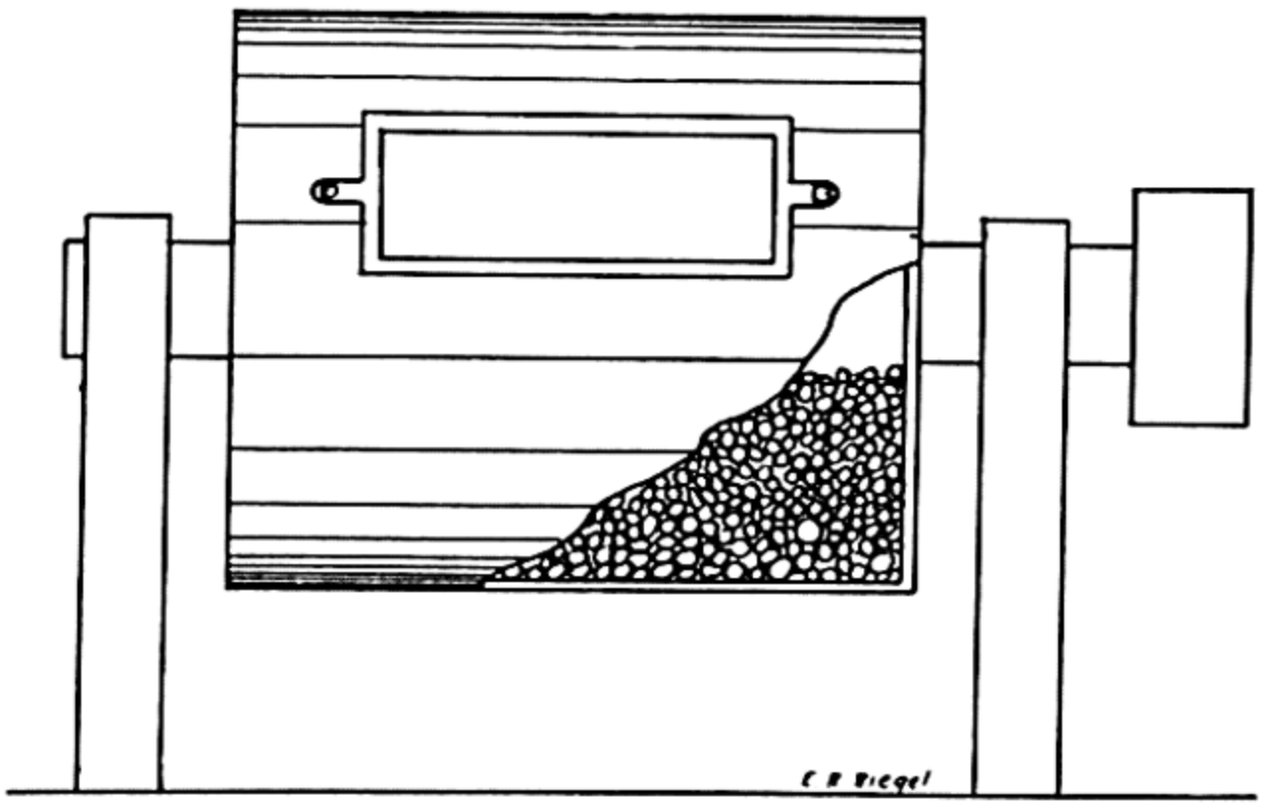


FIGURE 313.—A pebble mill for intermittent operation.

One industrial mill is closely modeled after the simple mill above; a steel container, which may be tulip-shaped, replaces the porcelain jar; it carries three or four iron balls for a container 24 inches in diameter. The shaft passes through the long axis of the tulip, and is inclined at an angle of 45°.

The best-known pebble mill in the chemical industries has water-worn quartz pebbles about 2½ inches in diameter, as nearly spherical as possible; they occupy one-third the space in a hard steel cylindrical container 4 feet long, 4 feet in diameter or larger; revolving on its horizontal axis (*compare* Figure 313).

A batch of material is placed in the mill, the cover clamped down and the mill revolved at a speed of 60 r.p.m. After a period, the mill is stopped; the cover is replaced by a grid which permits the powder to pass, but retains the pebbles; the mill is revolved again and gradually discharged into the hopper beneath.

This periodic operation may be changed into a continuous one by feeding and discharging through the trunnions; such a mill is the Marcy.

The Hardinge continuous pebble mill is pear-shaped, with the long axis horizontal; the feed (and discharge) is through the trunnions. It revolves at rather higher speed than the cylindrical mill, and has several sizes of pebbles which "classify" themselves; this mill is used for example for pulverizing Florida phosphate rock after a preliminary treatment in a disintegrator.

A tube mill is a cylindrical pebble mill whose length is several times its diameter.

The Edge Runner. The edge runner is one of the older devices, still much used, but less than formerly. Its function is partly that of a pulverizer, partly of a disintegrator. It consists of two circular stones about three feet in diameter, and eight inches wide, running on the eight-inch face. (*See* Figure 314.) They are carried on the two horizontal arms of a

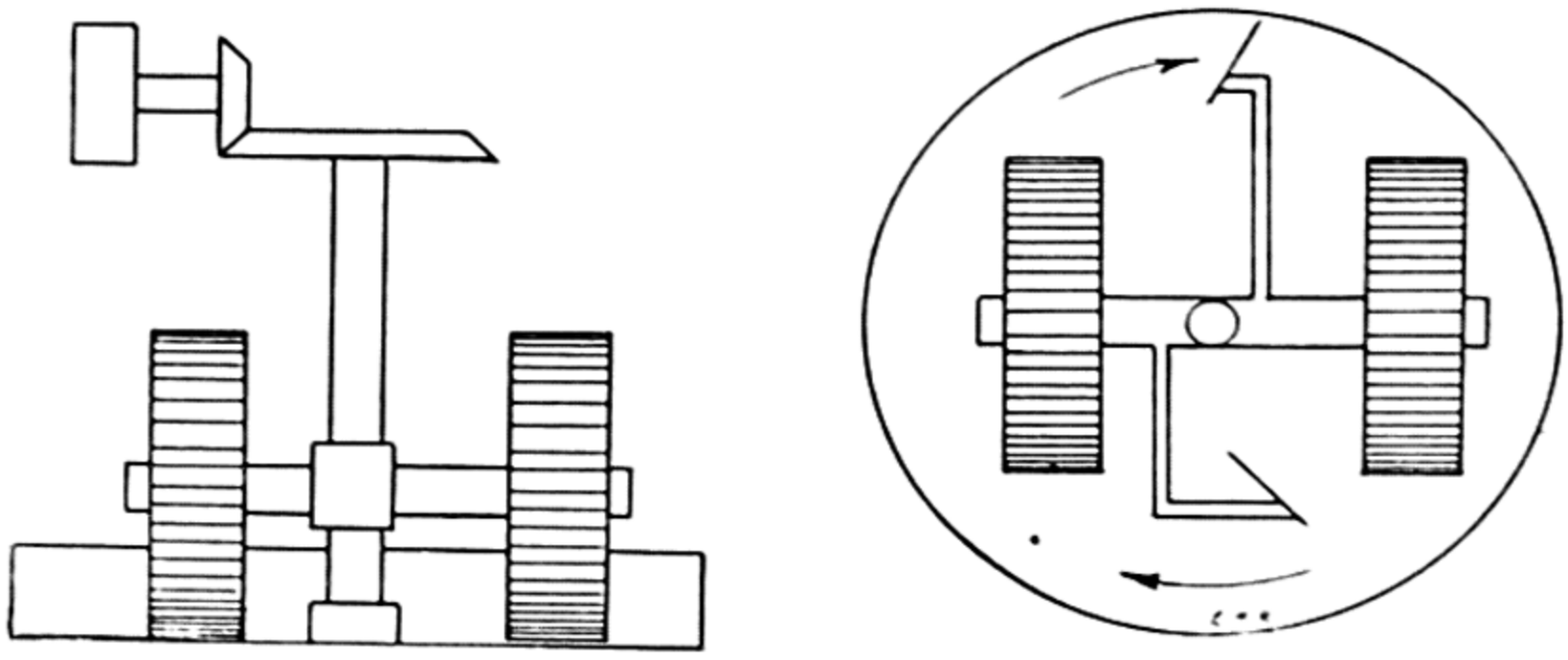


FIGURE 314.—The edge runner.

vertical shaft, and are placed on opposite sides. As the shaft rotates, the stones are pulled around, and as the line of travel constantly leaves the the vertical plane of the stones, there is a side-wise drag which grinds, in addition to the crushing due to the mere weight of the stones. The material lies in a shallow pan; the operation is either batch operation, that is, intermittent, or continuous, by means of slight alterations. Small plows sweep the material into the path of the stones.

Instead of rotating the stones in the stationary pan, the stones may be left stationary, and the pan rotated; also, corrugated steel cylinders of similar proportions may be substituted.

CHOICE OF APPLIANCE AND SEQUENCE OF OPERATIONS

Crushing operations frequently involve two or more devices; for instance, in a coke plant, the coal passes crushing rolls first, and the product is sent

to a Gardner crusher, of the rotary hammermill type, which reduces the egg size to a coarse powder; this is then loaded into retorts. In a gypsum plant, the rock from the mine passes through the gyratory, then the Jeffrey, and finally the Raymond mill; by these three steps, lumps of rock are reduced to an impalpable powder. Sometimes a single device is sufficient, for instance when sodium sulfide melt is made into cakes about three feet square and six inches thick, such a cake may be broken in several pieces by a sledge hammer, and the pieces fed to a jaw crusher set for rather fine crushing; the product is fine enough for leaching tanks.

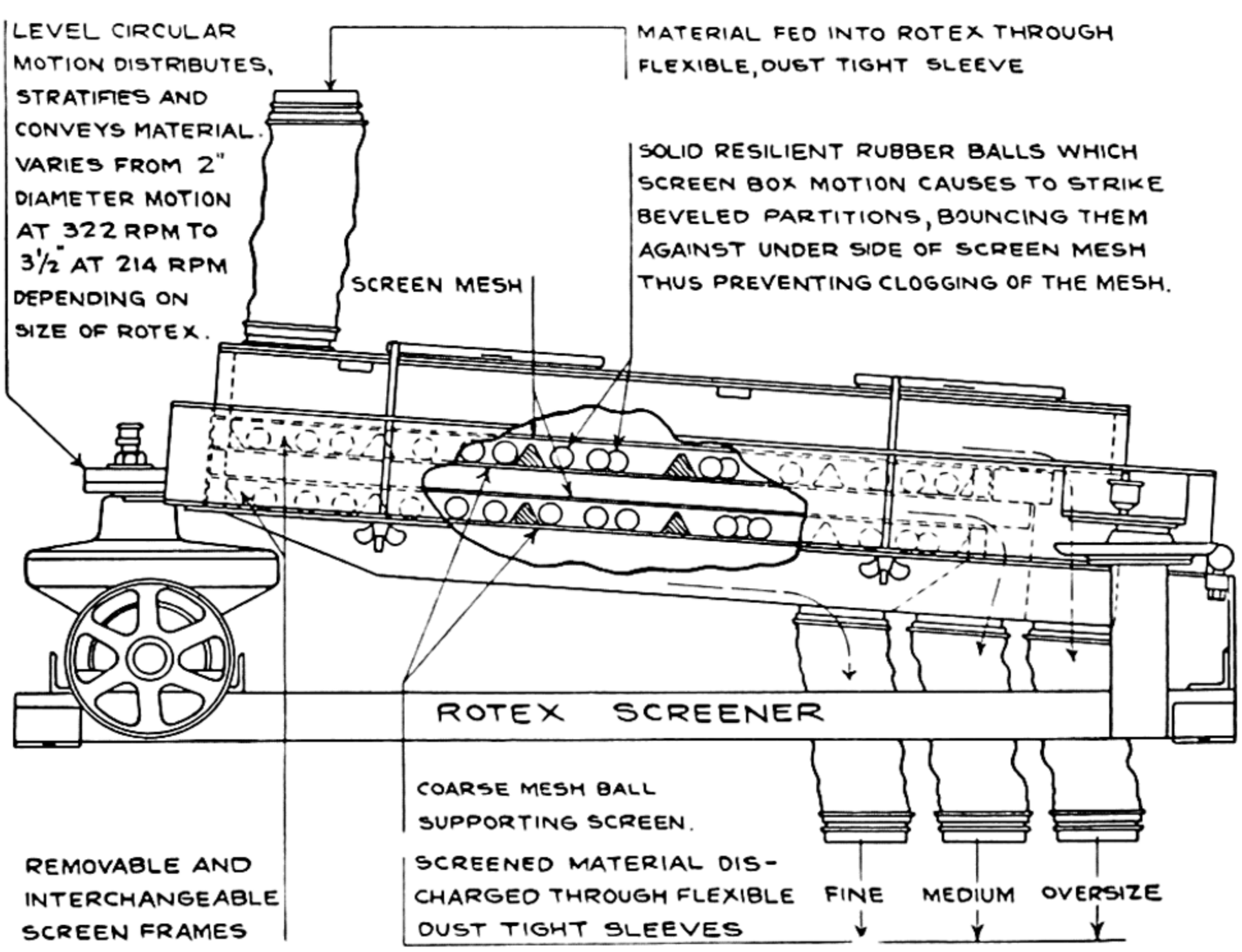


FIGURE 315.—Flat screen with rapid rotary jerky motion, and with tapping. (Courtesy Orville Simpson Co., Cincinnati, O.)

The choice of the crushing, disintegrating, or pulverizing device depends chiefly upon the desired fineness, but other factors must be considered. One is the toughness or brittleness of the material; another is whether very few fines are desired, or the greatest possible amount, with few coarser pieces. From any device, a single size is not obtained, but an assortment; to obtain one size, screens are used; the total product of the crusher is run over the screen; that which passes through proceeds to the next operation; that which remains on the screen, the tailings, returns to the crusher.

Screens. For small operations, a hand screen is used; it may be made by tacking a wire netting to a four-sided wooden frame. Placing the material in it and moving the whole mass back and forth, a part of the solid will pass through and a part will remain on the screen, if properly chosen. In all screening operations of the automatic type, some motion is required,

otherwise the mass lies on the screen and clogs it. Some automatic screens achieve this motion by revolving and so moving the solids; others are inclined, stationary, but receive rapid blows which constantly dislodge the material, causing the tailings to roll down the incline. The Moto-Vibro screens of the Sturtevant Mill Company are of this type. Usually three sizes are sorted by means of two screens, the coarser screen being placed over the finer one. The fines pass both screens; the middlings pass the upper but not the second; they run to the low point where a chute or a screw conveyor transfers them to the next device; the tailings cannot pass either screen and are returned by means of a chute and a bucket elevator to the disintegrator.

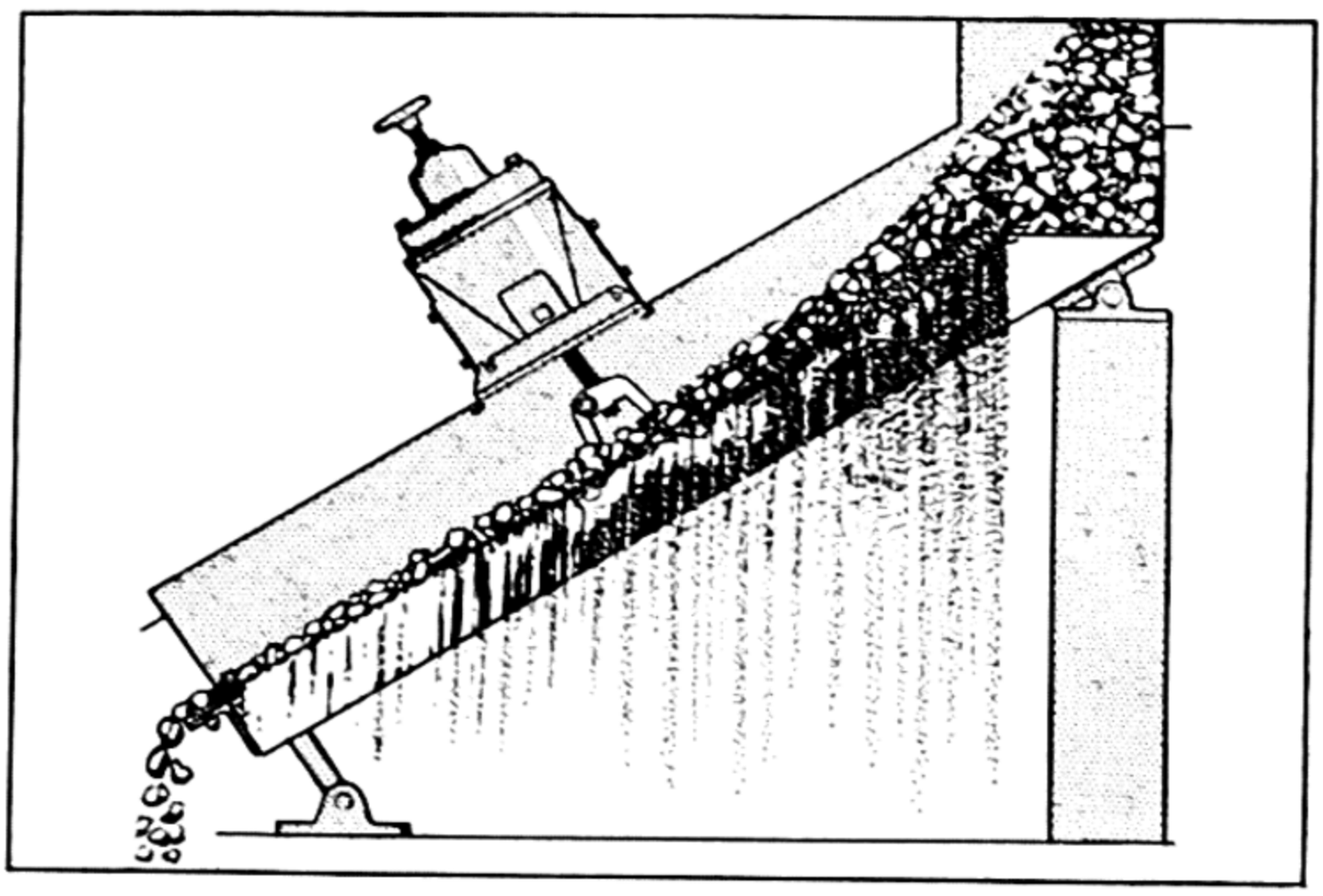


FIGURE 316.—Cross-sectional drawing of a one-deck electrically vibrated screen, the Hum-mer, showing the principle of operation. The stratification of the materials causes the fines to hug close to the screen, while the coarse particles travel on top. (Courtesy The W. S. Tyler Company, Cleveland, Ohio.)

The mechanically developed vibration may be a "positive circle throw" motion, or a reciprocating motion. A number of screens are electrically vibrated. For the fine sizes, the grading may be done by *air separators*, which sort by the floating quality of the particles; example, the Sturtevant Air Separator. The air separator is valuable especially in closed circuit grinding in which the suitable fines are collected and the tailings returned to the mill.

In the Blutergess high speed turbine sifter, a still different principle is applied. There is no shaking, no vibrating, no suction. The material is thrown by a central turbine against the cloth. The motor is $1\frac{1}{2}$ h.p.; the surface of the stationary screen is $6\frac{2}{3}$ sq. feet; yet the capacity is high. With a speed of 740 r.p.m., and a 110-mesh screen, 550 pounds of precipitated sulfur are screened per hour. With 1400 r.p.m., and a 60-mesh screen, 2000 pounds of aluminum stearate are delivered through the screen per hour.

The *rotary screen* may be cylindrical, of the same diameter throughout, when it is usually given a slight incline toward the discharge end. It is

mounted by slender arms to a central shaft, which is rotated slowly.[2] The material is fed to the inside of the screen; as the screen rotates, the solid travels further and slightly down; the fines pass through the meshes. If the screen has two sizes, the smaller mesh is first; using hypo crystals as an example, the fine powder would pass through first, the pea size and the lumps would roll on. At the second size mesh, the pea would drop through and would collect in barrels, free from either fines or lumps. The lumps pass all the way through the cylinder, and drop off at the lower end.

Instead of being cylindrical, the screen may be wider at one end than at the other; the material enters at the narrow end, and as the screen rotates around its horizontal shaft, it moves downward toward the wide end, where the tailings are discharged. Such screens are used for heavy materials such as gypsum rock or pyrite.

Other Patents

U. S. Patent 1,859,499, rotary drum ball mill in which pulverized material is removed by a current of air or fluid; 1,879,479, ball mill for carrying out reactions in the nature of sulfur fusions; and 1,862,557, same; 1,840,380, pulverizer of the rotary beater type; 1,862,889, a rotary crusher with screening grid; 1,888,636, cylindrical screening and concentrating apparatus having rotary motion; 1,882,908, inclined vibrating screen; 1,819,049, horizontal rotary screen or trommel; 1,798,433, rock crusher having an eccentric operating mechanism, and a shaker screen having its receiving end mounted on the eccentric of the crusher; 1,884,316, crusher of the rotary type applicable to furnace constructions; 1,874,830, jaw crusher consisting of a movable and a fixed jaw; 1,872,233, hammer mill crusher; 1,847,859, a double roll crusher; 1,871,727, apparatus for disintegrating particles suspended in a liquid; 1,764,138, hammer mill which has a series of hammers which crush the material as it moves along on a belt (does not have cage bars); 1,762,727, grain disintegrating mill consisting of one movable and one fixed attrition plate.

Reading References

"Principles of chemical engineering," W. H. Walker, W. K. Lewis, W. K. McAdams, and E. R. Gilliland, New York, McGraw-Hill Book Co., 3rd ed., 1937.

"Chemical Engineering Catalog," issued annually by the Reinhold Publishing Corporation, New York, should be consulted for general information on available appliances described in the Chapters 41 to 44 of this book.

"Crushing and grinding," W. F. Carey, *Trans. Inst. Chem. Eng. (London)*, 12, 179 (1934).

"Crushing and grinding appliances, the connection between type and purpose," B. W. Holman, *Trans. Inst. Chem. Eng. (London)*, 12, 186 (1934).

A number of articles on the theory and laws of crushing will be found in the *Trans. Am. Inst. Min. Engrs., Trans. Can. Min. Inst., Eng. Min. J., Trans. Ceramic Soc.*, and others.

"Screens in the process industries," Albert E. Reed, *Ind. Eng. Chem.*, 30, 1369 (1938).

"Electrostatic separations of solids," Foster Fraas and Oliver C. Ralston, *Ind. Eng. Chem.*, 32, 600 (1940).

"A review of certain unit processes in the reduction of materials," J. C. Farrant, *Trans. Institution Chem. Eng. (London)*, 18, 56-75 (1940), with an appendix on "The dynamics of screening," by R. F. Davis, p. 76.

[2] About 60 r.p.m. for a screen 36 inches in diameter and 140 inches long.

Among the many tasks which devolve upon the chemical engineer is that of finding vessels in which the reactions of commercial importance may be run. The requirement is never that the vessel should last for many years, but merely long enough so that its cost may be absorbed by the process; it follows that a cheaper vessel may be replaced more often than a dearer one, and that a valuable product will permit a more expensive reaction vessel than a product selling for a low price. A second consideration is that the time lost for replacement must be as short as possible, for while the plant is idle it earns nothing.

Chapter 45

Materials of Construction Used by the Chemical Engineer

The materials used by the chemical engineer are very numerous; of first importance are steel, cast iron, wood, stone slabs, bricks of various kinds, lead, copper, and stoneware. These materials serve for the construction of reaction vessels, absorbing and collecting vessels. The subject of bricks is inseparably connected with the cement in which they are laid; the cement must resist the attack of the reaction mass as well or nearly as well as the bricks themselves. Of secondary importance in point of tonnage are the special alloys such as "Duriron," "Monel" metal, bronze, quartz, glass-lined cast-iron vessels, and others. A third class of substances is the filling materials in towers for the absorption of gases in water, or for the drying of gases by means of sulfuric acid for example. A fourth class might be that of the catalysts, such as platinum and iron. A fifth class is the adsorbents, such as charcoal in the Burrell process for the removal of gasoline from natural gas. All these classes are used by the chemical engineer; the divisions are for the sake of clarity chiefly. But besides making the material, it must be shipped, and suitable containers are essential for the full development of a manufacture; glass, lead, steel, wood, absorption in diatomaceous earth, even wax, are concerned in the development of shipping containers.

Unlined steel is used wherever possible; storage tanks of considerable size are built of mild steel sheets, riveted or welded; the sheets with proper curvature and with the rivet holes punched, are shipped by rail and assembled on the spot, so that there is no limiting size in transportation which interferes. With cast iron, it is different; unless the piece is made in sections, bolted together on the job, its size is limited by the size of the railway cars. Unlined steel is used for the storage of oils, ammonia liquors, alcohol, concentrated sulfuric acid, mixed acid, and oleums, besides countless other liquids; it is the reaction vessel for the recovery of ammonia from the ammonium chloride liquors in the Solvay soda process, for the distillation of industrial alcohol and methanol, for the soda wood-pulp digester, and many others. Cast iron is used for caustic[1] pots, for the final con-

[1] References to other chapters would be so numerous in the discussion of materials used by the chemical engineer that they will not be given; the reader will please consult the list of chapters at the front, or the index.

centration to the anhydrous condition over the free flame; for nitric acid retorts, and Mannheim furnaces for hydrochloric acid; for the nitration and sulfonation of benzene and other organic substances; and for many other reactions. Cast iron is not as strong as steel, which is one reason why it is generally greater in wall thickness. It has, however, this great advantage, that it can be cast to any curved shape desired, and may have fins, internal weirs, and partitions. If the casting is to be water-cooled, internal passages may readily be arranged to permit the necessary circulation. Castings are comparatively cheap.

Castings (Iron). In a foundry, pig iron is the main raw material; it is chosen of a specific quality, and a certain definite proportion of steel scrap is added which among other things lowers the carbon somewhat. The pig iron with added steel is melted in a cupola, essentially a small blast furnace with an hourly capacity of 10 to 15 tons. The fuel is coke, and a small amount of flux (limestone) is provided, whose function it is to form a slag with the ash from the coke and any sand adhering to the pigs. The iron passes through the cupola practically unchanged in composition; the carbon, combined and free, remains the same; the silicon decreases somewhat, the sulfur increases slightly. The loss in iron is 5 per cent, chiefly as globules mixed with the slag.

The melted iron is drawn into ladles carried by overhead cranes (electric), and poured into the prepared form. Small castings are made in "flasks," two-piece boxes filled with sand in which the impress of the design is half in one part, half in the second part; the inner part of the casting which is to be hollow, is represented by a solid shape of sand, the core; where the core is, the metal cannot flow; it can only fill the space between the core and the flask. Flask and core are made from a pattern made of wood, from accurate measurements, with enough oversize to allow for the shrinkage of cast iron on cooling, one-eighth inch per foot. The small castings are poured from a crucible on long bars carried by two men; the crucible is filled from the ladle. The core is made to hold together by moistening the sand with molasses and baking till hard.

The practice in making a casting may be further illustrated by a caustic pot, which is cast right side up, that is, with the flange on the top and the round bottom at the base. There is first constructed a core, which is so large that bricks as well as sand are employed; around the core, a mold provides the outer wall which determines the outside surface of the casting. An extra height is provided in which the metal rises, carrying in its upper portions any slag which it may contain (the riser); this part is later sawed off. The metal flows into the comparatively thin space so provided, and fills it. After some cooling, the outer wall pieces are knocked down or lifted up (annular shapes); the pot may then be lifted in turn, and then the core knocked out.[2]

Castings are cleaned of core sand by sand blasting or by wire brushing, and may be machined on lathes; they may be drilled and threaded. Cast-iron drillings are short, almost powdery; steel drillings are long spirals or shavings.

[2] *Compare article in Chem. Met. Eng.*, 20, 394 (1919), with 8 illustrations

Steel. The steel used for storage tanks, car tanks, stills, reaction vessels, settling tanks, classifiers, evaporators, and an endless number of purposes is generally mild steel, with 0.20 to 0.30 per cent carbon. The thickness varies with the size of the vessel and the purpose. For a storage tank for alkaline liquor, 20 feet in circular diameter and 20 feet high, the sides would be three-eighths inch, the bottom perhaps one-half inch in thickness. Steel tanks are riveted, single or double, and caulked by a

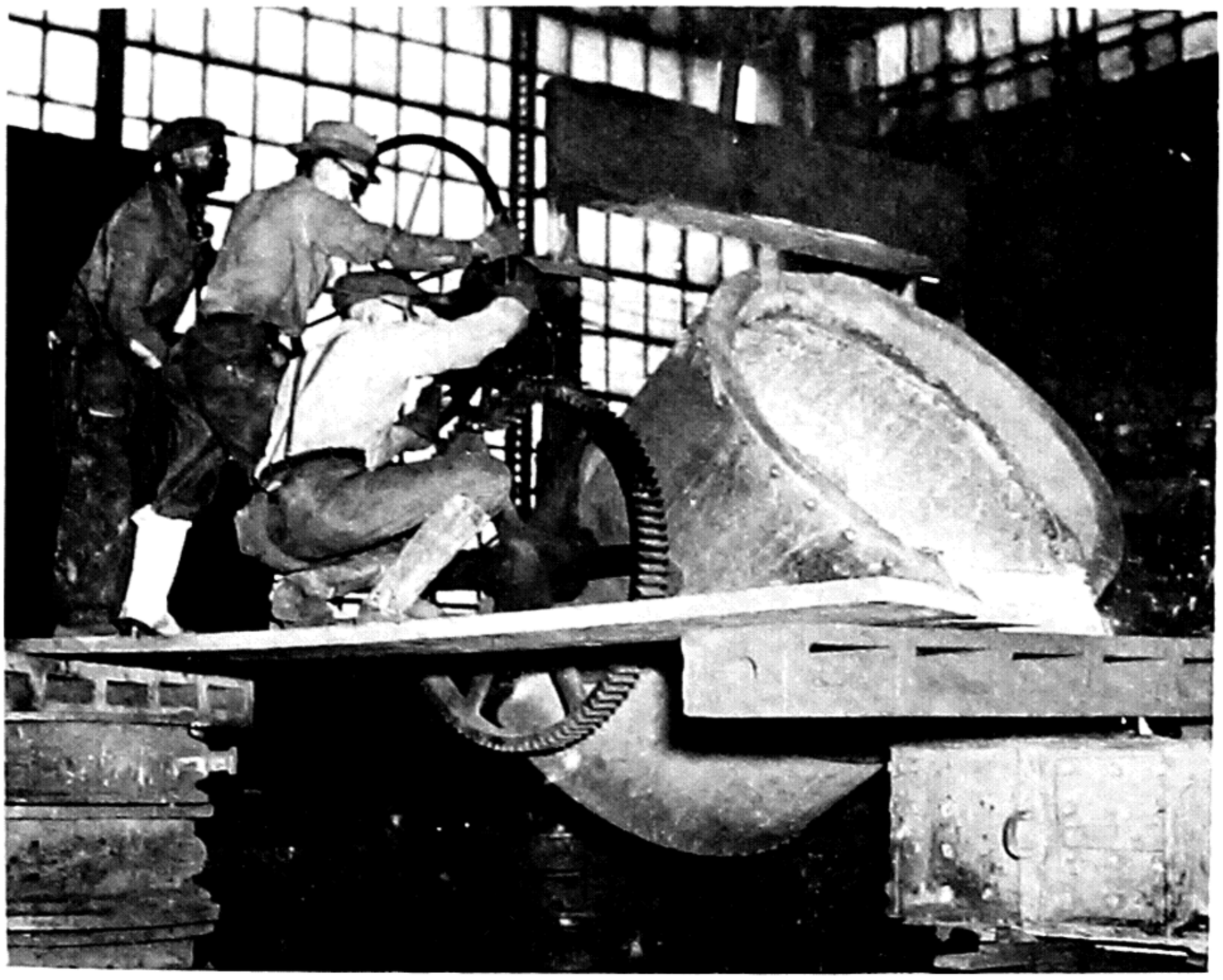


FIGURE 317. — "Near the end of the ladle"; pouring metal for a large casting (special cast iron). (Courtesy Buflovak Division, Blaw-Knox Company, Buffalo, N. Y.)

pneumatic chisel. The practice of welding instead of riveting is growing constantly; the weld has the advantage that it does not need caulking, and is not subject to a leaking rivet. Steel tanks exposed to the weather are painted on the outside.

Steel may be punched, as well as machined; it may be drilled and threaded; it may be bent into box-like shapes, cutting for the corners and welding the edges; two such boxes, one shallow and one deeper, are riveted together to form a jacket through which water may be circulated, the water-cooled jacket, suitable for furnace walls without any protection. Inhibitors of corrosion are briefly mentioned in Chapter 1 (*see also* reading references there). The suitability of steel to certain strengths of sulfuric acid will be found discussed in the same chapter.

Steel castings are poured from the bottom of a ladle; the molds may be hand-made or machine-made. Hand-made molds take longer to prepare and are used for larger pieces. The steel is prepared in an open-hearth furnace, most generally a basic open hearth, with capacity of 20 tons, for example; scrap steel with some pig iron makes up the charge. Additions are made in the ladle (Compare Chapter 48). A cast steel may run from 0.25 to 0.35 carbon, with specified amounts of manganese. In one plant, the molten steel is 3000° F. (1649° C.) in the furnace, 2700° F. (1482° C.) when poured. After cooling the casting is reheated, cooled to a definite temperature, and quenched in water (or oil) for a specific number of seconds. Cast steel may be forged. Certain pieces are carburized.

Wood. Formerly wood was used much more than now; whenever permissible, the steel tank has taken its place. For some processes, in which dilute mineral acids are used, wood (oak) is still the best material; for example in the extraction of bones with cold dilute hydrochloric acid for gelatin and glue making. For intermediate water storage in large plants, wooden tanks are freely used. A wooden tank is made tight by swelling it with water, and it will remain tight if kept filled; but if allowed to become dry, the planks shrink, and leaks develop; in this respect the wooden tank is inferior to the steel tank. Wooden tanks lined with lead are used for storage, crystallizers, and other purposes. The present war conditions (1942) have stimulated the use of wood for many chemical purposes.

Stone Slabs. Towers for the cooling of hydrogen chloride and for its absorption in water to form hydrochloric acid may be constructed of stone slabs. Sandstones about 6 inches thick and 4 or 6 feet square are placed for several days in hot tar which penetrates into the stone a short distance and renders it acid-proof; a stone 7 feet square 12 inches thick forms the base; it is hollowed out enough to give drainage to the discharge opening at its center. The bottom stone is placed on piers, and the square tower is built up of the thinner stones, each course consisting of two 4 by 4 and two 6 by 4 stones, held together by cast-iron corner pieces and steel rods. The joint between the stones may be filled with asbestos cord, or with specially made rubber gaskets. Such towers are not used as much as formerly, but many are still in operation. Every Mannheim furnace has at least a cooling box for the gas made of tarred stones.

Bricks. The common red brick and the sand-lime brick are used for piers and outside courses; soft or hard firebricks for the lining of fireboxes. The latter are also the more common acid-resisting bricks; they are strong, hard, and tough, and unaffected for example by the acid liquor in the sulfide pulp digester. In this digester, the bricks are laid in litharge and glycerin for cement; this mixture hardens and resists the acid liquor as well as the bricks. Until its introduction, the digesters had to be relined at frequent intervals, a costly interruption. In fireplaces, the bricks are laid in moistened fire clay, or in fire clay and silicate of soda solution. Sand and silicate of soda are also useful, and sometimes for filling cracks between bricks in a hot furnace (with alkaline charge), sand alone; it is gradually fused by the alkali and runs into the spaces between the bricks.

Portland cement with sand is used in the outside courses, unaffected by the furnace charge, but may also be used in numerous cases inside the furnace. Ground asbestos in silicate of soda is both fire-resisting, and to a considerable extent acid-resisting; for nitric acid, a little linseed oil is incorporated. Some silicate of soda mixtures protected by trade names contain, besides ground asbestos and silicate of soda, some tar. "Acid-proof" cement, sold as special cement under that name, is usually ground flint, which the customer is directed to mix with silicate of soda solution; fire clays and ground asbestos may be equally suitable.

Portland cement furnaces are usually lined with bauxite bricks, but recently unfired chemically bonded magnesia bricks have been used for this purpose. Magnesia bricks for basic Bessemers and similar processes are very resistant to slag and fused limestone. Chrome bricks are as dear as magnesia bricks ($100 to $200 per thousand); they are said to be neutral; slag does not cling to them.[3] Somewhat cheaper alkali-resisting bricks are made from alunite.

The function of all the bricks given above is to resist heat and chemicals; a brick may be needed, however, for a totally different purpose, namely, to divide a heating chamber from a reaction chamber; in this case, it may still need to be heat-resisting, but it must also be reasonably heat-conductive. Silica bricks are such, discussed in Chapter 10, where crucibles are also discussed; it should be added that shapes, slabs or bricks made of alumina or silicon carbide are also heat-conductive, and are available, though at higher cost than silica.

Lead. It may be said that it is to lead that the chemical industries owe their success. Until it was employed for the reaction vessels in the manufacture of sulfuric acid, the latter product was a curiosity; it is now a commodity at 1 cent, in favorable cases 0.5 cent per pound, and even less. Lead sheets form the walls of the sulfuric acid chambers, of the Gay Lussac and Glover towers, of the storage tanks, with wooden or steel frames, for the piping of the acid, for pumps, and for the conveyance of the gases from one tower to another perhaps distant one. The lead chamber walls are supported on wooden (also steel) frames, and the sheets are burned together, that is, the edges are melted together with a hydrogen-air flame. Lead-lined steel is used for the saturation of soda ash suspension in the manufacture of anhydrous bisulfite of soda, for the pickling bath in the galvanizing plants (if sulfuric acid is the pickling acid), in ammonium sulfate saturators, and in numerous other installations. Lead sheets which have become perforated, or thin in spots, are sent to be rerolled for a nominal charge, into any thickness desired.

Lead used for chemical purposes such as those listed above is soft lead; it is not the purest lead, but contains antimony, copper, zinc, and other impurities which render it more acid-resisting. By raising the antimony content to 6 or 10 per cent, the lead is made rigid, about twice as

[3] In normal times, a firebrick good for 2600° F. costs about $47; good to 3200° F., $85 to $100; size in both cases $4\frac{1}{2} \times 9 \times 2\frac{1}{2}$ inches; silica bricks, $58 and over. All prices for 1000 bricks, f.o.b. brick yard. Fireclay costs $9.80 per ton (for bulk). (Compare Chapter 10.)

strong as chemical lead, and remains acid-resisting. Lead-lined vessels, pipes and fittings, are also in use.

Copper. Copper is used for the redistillation of acetic acid, which does not attack it except to a slight degree; copper is used also for the steam coils in crude methanol stills, and for the rectification of ethyl alcohol. Copper is the melting vessel for a number of copper alloys; the varnish kettle is made of copper. Shelves and trays in the fractionating towers for liquid air, as well as for bubble towers in oil refining, are made of copper. Water-cooled copper coils are used in electrolytic furnaces, while water-cooled copper or copper alloy discharge pieces are suitable for fused sodium sulfide and other furnaces.

Stoneware. For acid vapors and acid liquors, stoneware furnishes cooling, absorption, and collecting vessels; it is made of selected clays, screened of all coarse particles, and sintered throughout its thickness; a strong material results, which may therefore be made with thin walls, and correspondingly more elastic and more efficient in cooling action. For mere storage, with no temperature changes, the vessel walls are made thicker. Some further information will be found in Chapter 10.

Hard Rubber. Hard rubber piping, pumps, and pistons have been applied with success in a number of cases; as example, hydrochloric acid may be pumped from one place to another one-quarter mile away by means of a small hard-rubber power pump and hard-rubber piping. Hard rubber may be threaded, and the threaded pipes put together with unions and sleeves; still another advantage is that hard rubber may be softened by hot water. It remains unattacked by almost any acid; hydrofluoric acid does not attack it.

Rubber-lined steel tanks for pickling, rubber-lined car tanks for hydrochloric acid, and rubber-lined pipes and fittings are widely used and absolutely reliable. "*Vulcalock*," for example, is a multilayer lining which unites upon curing. It is built up from the metal wall with rubber cements, soft rubber sheets, hard rubber sheets, and again a multiplicity of soft rubber sheets, to a thickness of $\frac{1}{4}$ inch or so. The bond to the metal is perfect. A brick lining may be installed to protect the rubber for certain uses.

"Duriron." "Duriron" is a cast iron with abnormally high silicon content, namely 14 per cent; it is practically unaffected by sulfuric or nitric acids, and only very slightly by hydrochloric acid. The drain pipes from sinks in large laboratories are made of "Duriron," which resists completely the action of the dilute solutions of all kinds of chemicals. Generally the bleacher in any nitric acid plant is made of "Duriron," for this material has the passivity of stoneware combined with almost the strength of cast iron, and a thermal conductivity surpassing that of stoneware and approaching that of cast iron. Acid lines are frequently "Duriron," and in general, this alloy has been a boon to the chemical industries. "Tantiron" and "Corrosiron" are essentially similar high-silicon cast irons, and serve similar purposes.

"Duriron" is extremely hard and brittle; it must be reinforced in many instances by a cast iron or steel envelope or frame. It cannot be machined,

drilled, or threaded; in order to face two flanges so that they fit they must be ground with abrasives, a tedious and expensive process.

"Monel" Metal. This white metal contains 67 per cent nickel, 28 per cent copper, and 5 per cent other metals, but no zinc, tin, nor antimony. It melts at 2480° F. (1360° C.), higher than cast iron or copper (specific gravity 8.87 cast). It is unaffected by common salt solution, while cast iron, steel, and copper are attacked. With many other chemicals it is comparatively inert, although it does not resist acids as well as duriron does; but "Monel" metal has the great advantage that it can be drilled and tapped, and in general handled in the machine shop as steel is. It may also be cast. The tensile strength of "Monel" metal is greater than that of mild steel and equal to that of medium steel.[4]

"Monel" metal may be drawn into wire, and the wire woven into cloth which may be used in the filtration of alkaline slurries. Iron wire cloth is used for the same purpose, but is less durable.

"Monel" metal is much more expensive than iron or steel, but in spite of this, its use has been expanding. Rotary dryers for salt (NaCl) (55 feet long, 6 feet in diameter, for example) have been lined with "Monel" metal plates, held in place by bolts of the same material. In refrigeration plants, all parts which come in contact with the brine give better service if made of monel metal. For the handling of sea water (on board ships) it is made into pump linings and pump rods; propellers of all sizes have been made of monel metal.

Chromium Alloys. Chromium steel and iron find several important applications in the appliances of the chemical engineer. The alloy consisting of iron and 13 per cent chromium resists the corrosion of water, salt water, and a great number of other liquids; it is often called stainless steel. It serves in the form of pipes, valves, autoclaves, and other containing vessels, also in making cutlery. As an example of the wide range of possibilities, it might be stated that the 14 per cent chromium alloy with 0.15 per cent carbon resists nitric acid of any concentration at any temperature below the boiling point; it has been found suitable as the structural material for reaction and absorption towers in the ammonia oxidation process.[5]

Not only the chromium-iron alloys, but chrome-plated steels are very resistant to corrosion, so that chrome plated pieces of large sizes are now used by the chemical engineer. As example, the vaporizing chamber in the thermal process for cracking oil for gasoline might be given. Plated tableware and automobile fixtures are very beautiful, with a high luster and

[4] For tensile strength of steel, *see* Chapter 48; monel metal has 90,000 pounds per square inch, for tests on rods (booklet on Monel Metal, by the International Nickel Co., New York).

[5] An electronic theory for the development of passivity in a chromium iron alloy for example states that an electron in the "s" level of the iron migrates to the available "d" level, which can accommodate five electrons, of the chromium atom, and that this adjustment is the source of passivity or non-attack by acid. The theory permits an estimation of the amount of alloying element the iron alloy should have, and the estimate agrees closely with the alloys used in practice. "The nature of passivity in stainless steels and other alloys," parts I and II, by H. H. Uhlig and J. Wulff, *Amer. Inst. Min. Met. Eng.*, 135, 494 (1939); part III, by H. H. Uhlig, *ibid.*, 140, 387 (1940).

TABLE 146.—*Composition and corrosion-resistance of some chromium alloys.*

Alloy	Composition	Resists
Allegheny metal	Fe; Cr 17-20; Ni 7-10; Mn <.5; S <.5; C <.2	H_2S, SO_2, oxides of N, HNO_3, NaOH, NH_4OH
"Duriron" (not machinable)	Fe; Si 14.5; C .85; Mn .35	H_2SO_4, HCl, HNO_3, HAc, NaOH, NH_4OH, Cl in Aq. sol.
"Elcomet K"	Ni 22; Cr 23; Cu 3.5; Mo 2; W .13; Fe 48; Si 1.25; Mn .50; C .12	Corrosive mine waters in coal mines; any acid liquor.
R-55 (La Bour)	Ni 52; Cr 23; Cu 6; Mo 4; W 2; Fe 8; Si 4; Mn .50; C 25	Viscose solution in rayon plants.
'Hastelloy" A	Ni 60; Fe 20; Mo 20	Dil. cold H_2SO_4, dil. cold HCl, HAc, NaOH, NH_4OH
"Nichrome"	Ni 60; Fe 25; Cr 15	
Stainless A	Fe; Cr 14; C .35	HNO_3, HAc, NaOH, NH_4OH
Stainless N	Fe; Cr 18; Ni 8; C .18	HNO_3, HAc, NaOH, NH_4OH
Stainless steels	Fe; Cr 8 and over; Mn 4; C <.12	HNO_3, HAc, NaOH, NH_4OH
"Stellite" (not machinable)	Co 40-80; Ni 0.25; Cr 20-35; C .75-2.5	H_2SO_4, HAc (in absence of air), NaOH
"Monel" metal	Ni 60-70; Cu 25-35; Fe 1-3; Mn .25-2; C .5-3	SO_3, NaOH, HCl, H_2SO_4
Zirconium #200	Zr 2.77; Si 9.15; Ni 71.41; Al .32; Fe 12.03	

a bluish color; they do not tarnish. A number of alloys are described in Tables 146 and 147.

Fused Silica. A material totally unaffected by acid gases is fused silica, obtainable in many forms, among others in 4-inch diameter *S*-bends, suitable for the cooling of hydrogen chloride. Other shapes are recommended as absorbers of the same gas in water. Silica pipes withstand changes of heat better than stoneware, and are used for a first cooler (in the Mannheim) with good results, but otherwise its service is not markedly superior to that of stoneware, which is far cheaper. Silica is furthermore easily broken by an accidental blow.

TABLE 147.—*Corrosion tests on special material for comparison with zirconium alloys.*†

Sample	C* in 5 per cent HCl Aërated	C in 95 per cent H_2SO_4
"Duriron"	.....	0.00002
Cast steel	0.04468	0.00817
Cast iron	0.16298	0.00004
"Hastelloy" A	0.00437	0.00001
Zirconium, #200	0.00366	0.00006

† Taken from "Corrosion resistance of zirconium alloys," H. L. Coles and J. R. Withrow, *Trans. Am. Inst. Chem. Eng.*, *27*, 253 (1931).

* C = Corrosion expressed as inches penetration per month.

For the preparation of chemically pure water, a silica apparatus is well adapted.

"Pyrex" Glass by itself, and not merely as a lining, is fast taking a prominent place among the materials available to the chemical engineer. For example an all "Pyrex" distilling column, about 20 feet high, is available and offers the advantage of permitting the observer to follow the operations. The bells on the several plates are fastened down with "Pyrex" bolts and nuts.

Glass-lined cast-iron vessels combine the inertness of glass with the strength of cast iron; they are used for numerous evaporations and reactions. For the preparation of yeast cultures brass-lined tanks are indispensable. For many purposes, fair-sized enameled and glazed porcelain vessels may be improvised from slightly defective (in shape) bathtubs, rejected for the regular trade.

FIGURE 318.—Storage tanks for 40 per cent hydrochloric acid made of "Haveg," reinforced by outside wooden strips. (From the Bergius plant for Wood Hydrolysis, Heidelberg.)

Sulfur-containing cements, melting at a moderate temperature, may be flowed over the inside of a cast-iron vessel coating its walls, so that it becomes acid-resisting, for cold acids (basolite).

A material called *Mammut,* of German origin, has become of importance in the wineries, for coating the inside of wooden tanks as well as concrete ones, in which the grape juice and the fermented product is held. Mammut is black, resembles wax in appearance, is tasteless, almost odorless, and insoluble in the dilute alcoholic and acetic wine solution. The faint odor which it has is that of an odoriferous balsam.

The structural material "Haveg" consists of a phenol-formaldehyde resin

containing a selected asbestos filler. It is a strong material, and has the particular merit of resisting most acids of low and medium concentrations. Specific gravity, 1.6; compressive strength 10,400 lbs./sq. in.; unchanged in any way up to 130° C. (265° F.). It has a low heat conductivity. "Haveg" is made into tanks 10 feet high and 10 feet in diameter. Tanks for pickling iron, for electrolytic processes, for dyeing operations, are available of "Haveg." In many cases, a steel shape is covered with the resin and filler, combining the strength of steel with the inertness of the resin. "Haveg" does not resist acetone, strong oxidizers, pyridine, or sodium hydroxide.

Tower Packing. For the absorption of gases in water, towers may be packed with coke, an inexpensive packing. Broken stoneware may be used, or "rings," short cylindrical pieces of any desired diameter and of any material—stoneware, "Duriron" or other. For sulfuric acid, quartz lumps, with irregular shapes, and classified as to size, are used. Hollow spheres of stoneware have been proposed, while the so-called spiral chemical rings, in two sizes, 6 and 3 inches in diameter, have been very successful.[6] A good packing must offer maximum surface of the liquid to the gas, retain the descending liquid for a period long enough for saturation, and allow free circulation of the ascending gas. The Berl saddles excel in this respect; they are made of stoneware, porcelain, or other material.

Catalysts and adsorbents are discussed in their proper place in other chapters. The science of catalysis is rapidly advancing, but as yet many firms must make their own catalysts, because some of the catalysts are not as such on the market, even in a preliminary form. As adsorbents, charcoal and silica gel are best known; both have been applied to the removal of valuable gasoline vapors from natural gas. Silica gel is made[7] from silicate of soda solution (sp. gr. 1.185) by the action of hydrochloric acid (10 per cent), at the temperature of 50° C., with stirring. After setting 4 hours, the gel is washed free from salt with water and dried in a current of air at 75° to 100° C.; finally heated in a vacuum. Hard, transparent, porous granules result, with high adsorptive power. The gel is stable to 700° C. Only by observing certain definite conditions is the gel obtained in the active form, with high commercial value. Activated alumina is a partially dehydrated aluminum trihydrate, which can adsorb as much as 14 per cent of its weight in gases and vapors. As for silica gel, the alumina adsorbent must be reactivated by heating, to 350° to 600° F., followed by cooling before starting the next cycle. Activated alumina is furnished in granules which pass an 8 to 14 mesh, and other sizes. Silica gel is furnished in a similar size granule, and also, for certain adsorptions, in powder form.

Aids in filtration in the form of fine powders, usually natural powders such as diatomaceous earth, have been introduced under various names ("Silicel") and have proved of great help; they are stirred into the turbid liquid, and after some time the filtration is performed. The very fine, essentially colloidal particles of the turbidity are adsorbed by the added powder. The same powder frequently removes color as well as turbidity, but not

[6] Manufactured by the B. Mifflin Hood Brick Co., Atlanta, Ga.
[7] U. S. Patent 1,297,724 (1919), to Walter Patrick.

always; with oils, such as linseed oil and also wood-tar oils, fuller's earth (a clay) has reduced color.

Decolorizing agents include "chars," which were made originally by charring bone; the residual carbon is accompanied by a calcium phosphate substructure. In using these decolorizing agents, they are added and suspended in the solution to be cleared of color; after some time, the suspension is filtered. For acid solutions, bone char is objectionable, as some phosphoric acid forms. The "vegetable chars" and specially trade-marked articles do not contain phosphates. One of them is carbon with 40 per

FIGURE 319.—Diatomaceous earth from New York state, showing the fine structure which gives rise to large surface; run of mine sample, unselected. Micrograph as reproduced, 62 diameters. (Photographed in author's laboratory.)

cent fine sand which passes a 200 mesh sieve; the presence of the sand facilitates the suspension, and especially renders the subsequent filtration easy and rapid.

Plates for the filtration of very acid solutions, such as concentrated sulfuric acid, consisting of porous silica ware, have been received with favor ("Filtros"). A single plate is perhaps 10 by 10 inches; if a larger surface is desired, several plates are set in an acid-proof cement to form the roof of a box, to which suction may be applied to facilitate the filtration.

SHIPPING CONTAINERS

The mineral acids were shipped in former days in glass carboys of the balloon type, packed in hay or ground cork. For nitric acid, such packings are dangerous, and the Stahl carboy was developed, in which a 12-gallon bottle with straight sides is held in place by four strips of wood at the corners of the containing box; the surface of the strips (4 inches wide) is grooved to soften it. The dimensions of the box and of the bottle are so adjusted that the bottle can just be forced in place by gentle pressure. This style carboy was so successful that it has become standard for all acids.

Glass- and lead-lined containers were used exclusively for the shipment of sulfuric acid until steel tanks, portable and stationary, were introduced. This simplified the shipping of sulfuric acid and mixed acids, reducing the labor cost and the loss due to breakage; it took some time to convince customers that acid shipped in steel drums holding 2000 pounds or steel tank cars holding twenty times as much was as good as acid shipped in the familiar glass carboys.[8]

Single tanks on a railroad flat car, used for many years only for crude oil and petroleum products, have gradually become standard in nearly all branches of chemical manufacturing. Steel for sulfuric acid and mixed acid is well known. Anhydrous ammonia is shipped in car tanks of similar size; single units for liquid sulfur dioxide, and for liquid chlorine, are in daily use. A tank of aluminum for 98 per cent acetic acid has been adopted as well suited. Steel tanks with a thin nickel lining have been introduced.[9]

Light sheet-steel drums with tight covers are much used, also steel barrels, tight wooden barrels for liquids, sometimes paraffin-lined. Square lead boxes in wooden protecting cases are used for hydrofluoric acid, also ceresine bottles. Mercury is transported in cast-iron flasks. Many solids are shipped in bulk, or in sugar barrels (not air-tight).

There is promise at the present time that a drum of light weight with welded joints will be developed, of chrome-iron alloy (17 per cent Cr), in which nitric acid made by the oxidation of direct synthetic ammonia, hence free from halogens, may be shipped. Tank cars of the same material suitable for such nitric acids are now constructed. Welded steel barrels and drums are being developed especially for the brewery trade.

Other Patents

U. S. Patent 2,066,229, casting by the centrifugal casting process; 2,056,766, producing iron-chrome castings containing nitrogen; 2.066,229, casting by the centrifugal casting process; 2,056,766, producing iron-chrome castings containing nitrogen, to F. M. Beckett.

Reading References

"Materials used in chemical engineering operations," B. E. Roetheli and H. O. Forrest, *Ind. Eng. Chem.*, **24**, 1018-1027 (1932), very complete, tabular form, with illustrations.

"Corrosion of metals by phosphoric acid," P. R. Kosting and C. Heins, Jr., *Ind. Eng. Chem.*, **23**, 140 (1931).

"Corrosion resistance to zirconium alloys, Zirconium VII," H. L. Coles and J. R. Withrow, *Trans. Am. Inst. Chem. Eng.*, **27**, 253 (1931), with all previous references.

"Inhibitors in action of acid on steel," F. H. Rhodes and W. E. Kuhn, *Ind. Eng. Chem.*, **21**, 1066 (1929).

[8] Dr. Wm. H. Nichols said: "The first change from the carboys to iron or steel for sulfuric acid containers was a cylinder placed on a barge, capable of holding 50 tons of product. One small oil refiner was induced to put in a steel receiving tank, but for one whole year, a second one equally daring could not be found. It was feared not only that the acid would eat the container, and destroy it, but also that the acid itself would become weak." *Ind. Eng. Chem.*, 10, 768 (1918).

[9] Further details in "Regulations for the transportation by rail of explosives and other dangerous articles in freight, express, and baggage service, including specifications for shipping containers," Bureau of Explosives, 30 Vesey St., N. Y., Sept., 1930; and supplement #5, to Jan. 20, 1933. Similar data may be found in the Condensed Chemical Dictionary, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), 1941.

"Welding in chemical engineering," J. R. Booer, *J. Soc. Chem. Ind.*, **49**, 17T (1930).

"Tables of chemical compositions, physical and mechanical properties and corrosion-resistant properties of corrosion-resistant and heat-resistant alloys"—12 oversize tables bound in handy booklet form, published by the American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa., 2d ed. rev., 1931.

"Recent developments in corrosion- and heat-resisting steels," Sir Robert Hatfield, T. G. Elliott and R. N. Sarjant, *J. Soc. Chem. Ind.*, **49**, 41T (1930).

The division "Iron and steel castings," Richard Moldenke, in Marks' "Mechanical engineering handbook," New York, McGraw-Hill Book Co., 1916, pp. 449-519.

"Engineering properties of cast iron," E. A. Piper, *Iron Age*, October 18, 1934, an article which presents iron castings in a new light.

"Wood as a chemical engineering material," Clark S. Robinson, *Ind. Eng. Chem.*, **14**, 607 (1922).

"The principles and application of tower fillings," P. Parrish and F. C. Snelling, London, Ernest Benn, Ltd., 1927.

"Stoneware as a chemical engineering material," Percy C. Kingsbury, *Ind. Eng. Chem.*, **19**, 693 (1927).

"The building of containers for severe service," T. McLean Jasper, *Ind. Eng. Chem.*, **20**, 466 (1928).

"High speed agitation under pressure," A. H. Macmillan and N. W. Krase, *Ind. Eng. Chem.*, **24**, 1001 (1932).

"The handling of corrosive gases," T. H. Chilton and W. R. Huey, *Ind. Eng. Chem.*, **24**, 125 (1932).

"High pressure and temperature symposium," *Chem. Met. Eng.*, **37**, 530-591 (1930).

"High pressure and high temperature technology," N. W. Krase, *Chem. Met. Eng.*, **37**, 530 (1930).

"The celotex and cane-sugar industries, bagasse or sugar a by-product?" E. C. Lathrop, *Ind. Eng. Chem.*, **22**, 449 (1930).

"Quick-setting silicate of soda cements for acid-proof tank and tower construction," F. D. Snell and H. Farkas, *Ind. Eng. Chem.*, **23**, 521 (1931).

"The industrial application of active carbon," K. Evans, *Trans. Am. Inst. Chem. Eng.*, **7**, 134 (1929).

"Metallurgy from the standpoint of the chemical engineer," L. Singlehurst-Ward, *Trans. Inst. Chem. Eng. (London)*, **11**, 75 (1933).

"The course of liquor flow in packed towers," Theodore Baker, Thomas H. Chilton and Harcourt C. Vernon, *Trans. Amer. Inst. Chem. Eng.*, **31**, 296 (1935).

"Wetted surface in ring-packed towers," F. Mayo, T. G. Hunter and A. W. Nash, *J. Soc. Chem. Ind.*, **54**, 375T (1935).

"Pressure Storage of Gases and Liquids," R. S. McBride, *Chem. Met. Eng.*, **42**, 676 (1935); with 7 illustrations.

"Metals and Alloys used in the construction of chemical plant," James E. Lee, World Power Conference, London (1936), vol. I, paper B 11.

"Symposium on new metals and alloys applicable to the chemical industry," *Ind. Eng. Chem.*, **28**, 1366-1416 (1936).

"Protective coatings for metals," R. M. Burns and A. E. Schuh, New York, Reinhold Publishing Corp., 1939.

"Chemical Engineering materials of construction," *Ind. Chem. Eng.*, **39**, 1193-1264 (1947); the first of a series on this topic, to appear annually.

For the control of operations in industrial plants, the chemical engineer has at his disposal a fast-growing array of instruments; their relative values are best exhibited by grouping them together in one discussion.

Chapter 46

Instruments of Control Used by the Chemical Engineer

Hydrometers

The concentration of a solution, for instance of sodium thiosulfate, is allowed to proceed until the density reaches a definite point, which trials have shown to be high enough so that on cooling a rich crop of crystals will be formed, yet low enough to contain enough water to form a mother liquor which will carry away the impurities; that density, in this case 51° Bé. for the hot liquor, is determined by means of a hydrometer. In countless other similar preparations of liquors, similar tests are made with the help of the same instrument.

In the manufacture of sulfuric acid by the chamber process, the amount of steam or sprayed water sent into a chamber depends upon the strength of the acid drips; this strength is determined by the hydrometer. For any process of dilution or of strengthening of this acid, and many others, the same instrument is used.

The simplicity of the apparatus needed insures its continued use; a container, usually a glass or lead cylinder, the hydrometer proper, and a thermometer, form a complete set.

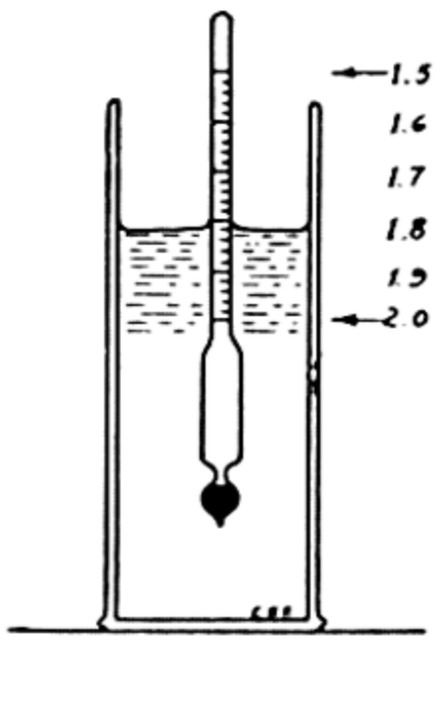


FIGURE 320.—Hydrometer for liquids heavier than water, for the range in specific gravity of 1.500 to 2.000.

Hydrometers for Liquids Heavier than Water. A hydrometer is a float, with a lower wide chamber which is suitably loaded with mercury or iron shot, and an upper tubular chamber in which a scale is provided. The float is buoyed up to a height depending upon the specific gravity of the liquor; the higher the specific gravity, the higher is the float pushed up. The point on the scale on a level with the surface of the liquid, after the instrument has come to rest, is read. The construction of the hydrometer is shown in Figure 320.

The "common" hydrometer reads from 0° to 72° Bé., and frequently carries the equivalent metric values, the specific gravities, from 1.000 to

2.000. The smallest division is one whole degree, and can hardly be subdivided; this instrument is therefore used for the first approximation, indicating which one of the finer ones should be used next. A scale of ten degrees Baumé forms usually one instrument of the more accurate type, each degree being subdivided into tenths; these are wide enough to allow an estimate to within 0.02° Bé., equivalent to about 0.005 on the metric specific gravity scale. Hydrometers graduated for specific gravity readings are coming into use more and more; for the finer types, the scale covers one-tenth (thus 1.200 to 1.300), subdivided in ten hundredths, and each of these in ten thousandths; each of these last divisions may be subdivided by estimation into fifths, giving a final reading to within 0.0002 on the metric specific gravity scale. Thus for the space from 1.000 to 2.000 there would be ten glasses; such glasses are usually kept in the plant laboratory and the samples to be tested are brought there.

In order to insure accuracy to the last estimated place, a set of glasses [1] standardized at the Bureau of Standards in Washington is kept in the laboratory for comparison only; a second set, the one in use, is compared with the standards and the necessary corrections listed on the cover of the containing box.

Temperature Corrections. Such accurate hydrometers would have no meaning if at the same time the temperature were not determined; this is usually done by means of the same instruments, which carry an enclosed thermometer reading from −10° to 40° C. or the corresponding values in the Fahrenheit scale. By means of tables, or in the absence of tables by means of determinations, a correction for temperature is applied, in order to reduce the readings to 60° F., the standard temperature.

For example, a sample of muriatic acid gave the reading of 21.6° Bé. at 74° F.; the correction for the range 22° to 25° Bé. is one-twenty-eighth degree Bé. to be added [2] for each degree Fahrenheit over 60°; hence

original reading	21.6
correction for error of scale	.0
correction for temperature 1/28 × 14	.5
	22.1

As the acid must be 22° Bé., in this case, it just passes.
Using metric specific gravities the corresponding values would be:

original reading	1.1751
correction for error of scale	0
correction for temperature 0.00035 × 14	.0049
	1.1800

For control within the plant, the accuracy is not so great; a liberal margin of safety is provided by making the goods intended for shipment distinctly overstrength.

[1] Such standard sets are usually the pride of the laboratory.
[2] For temperatures above 60° F. the correction is added; below 60° F., subtracted. 60° F. equals 15.56° C.

The relation between the Baumé scale and the metric specific gravity scale and a table for the Baumé scale for liquids heavier than water with the corresponding specific gravities is given in the Appendix.

Hydrometers for Liquids Lighter than Water. A water solution of ammonia decreases in specific gravity as its content of ammonia increases; the strength of the liquor is judged in this case also by means of a hydrometer which must be graduated in such a way that the further it sinks in the liquor, the higher will be the reading in degrees Baumé on the scale. This is therefore an entirely different Baumé scale, which is distinguished from the previous one by adding the words "for liquids lighter than water." The

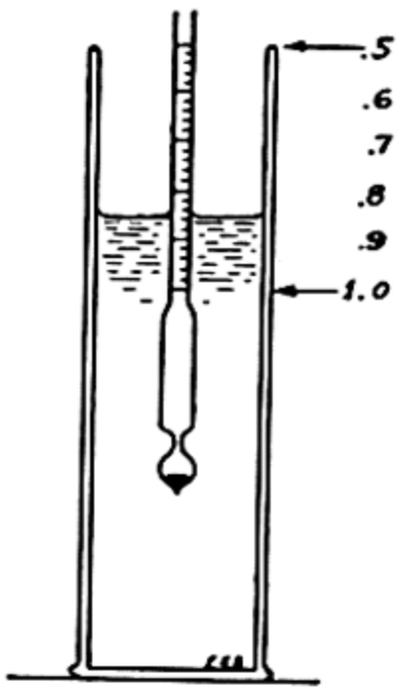


FIGURE 321.—Hydrometer for liquids lighter than water, for the range in specific gravity of 0.500 to 1.000.

corresponding specific gravities are less than unity. Such an instrument is shown in Fig. 321. A table giving the Baumé scale for liquids lighter than water with the corresponding specific gravities will be found in the Appendix.

A correction for temperature differing for each liquid must be applied; for temperatures above 60° F., it is subtracted.

TEMPERATURE MEASUREMENTS

For temperatures between −20° C. (−4° F.) and 360° C. (680° F.), the ordinary mercury thermometer is used widely, in spite of the fragility of the glass container. Such an instrument is really a dilatometer; the expansion of the mercury at the various temperatures is measured against the glass scale. A nitrogen-filled mercury thermometer will read temperatures to 550° C. (1022° F.); such instruments are made of special, hard glass, which fuses only at still higher temperatures.

Pressure thermometers, which may be gas-filled, vapor-filled, or liquid-filled, are widely used, and are comparatively simple instruments. The pressure developed in the vapor tube, for example, distorts a Bourdon gauge; the reading of the pressure becomes the measure of the temperature.

The application of the hand is also a practical method for judging moderate temperatures.

Thermocouples are used over practically all ranges of temperatures from that of liquid air (−190° C., −310° F.), to 1400° C. (2552° F.), which is the heat of a coal fire under forced draft. For temperatures between 500° C. (932° F.) and 1000° C. (1832° F.), resistance pyrometers, espe-

cially platinum ones, are valuable. For temperatures above 1000° C., in addition to thermocouples, radiation pyrometers, optical pyrometers, and Seger cones are used in industrial plants. These instruments may each be used over wider limits than indicated. The choice of instrument will depend not only upon its special adaptability for the temperature range to be studied, but also upon the danger of deterioration if immersion in a fused chemical for instance is required; the radiation and optical pyrometers would then be preferred as they have the advantage of being operated at a distance from the furnace or hot object.

A single observation may be required once in a while, or regular observations at stated intervals, or constant readings; the latter are now made from charts marked by recording pyrometers, on which not only the high and low points appear, but the temperature at every moment.

Thermocouples. When two dissimilar metal wires are joined in two places and one junction is heated while the other one remains cold, an electromotive force is set up in the system which is a function of the temperature at the hot junction, provided the cold junction remains at an even temperature. (*See* Figure 322.) Such pairs of wires are chosen as will remain

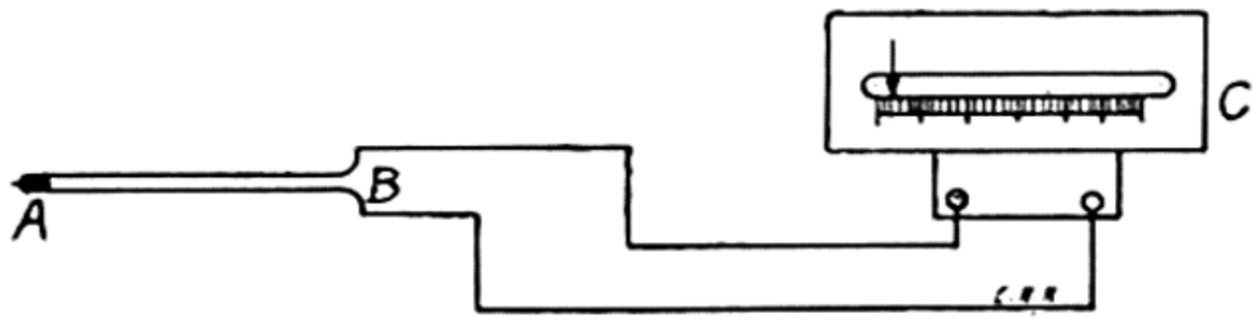


FIGURE 322.—Diagrammatic sketch of a thermocouple with millivoltmeter.

unaltered at the temperatures to be measured, and if several pairs are suitable, that pair is selected which gives the greatest increase in electromotive force for each degree rise; a third criterion, and not the least important, is the cost of the metals.

The electromotive force is measured on a millivoltmeter [3] which may be graduated in millivolts, or directly in degrees; if in millivolts, the degree corresponding to each reading is read off on a chart, on which the temperatures are entered as abscissæ, the millivolts as ordinates; for each thermocouple a separate chart is made by reading the electromotive force set up in two or more baths, or regions, of known temperatures; if graduated in degrees, a certain voltmeter must be used for a designated thermocouple, and the reading is direct.

The instrument in its simplest form is portable, and consists of the fire-end, which is the thermocouple proper, sheathed in an iron or porcelain protecting tube; two copper leads, and the millivoltmeter.

The electromotive force may also be measured by means of a portable potentiometer, in which the electromotive force set up in the thermocouple is matched by an oppositely directed electromotive force until a galvanometer needle shows zero current. Dry cells may be used for the matching current, and compared daily to a standard cell, such as the Weston. The

[3] With high or low internal resistance; the high internal resistance type has the advantage that even considerable variation in the leads has no effect on the reading.

potentiometer system for thermocouple currents is coming into increased favor; it is a little more complex than the millivoltmeter method, but no more than the platinum resistance pyrometer. It consists of the fire-end, the thermocouple proper, the copper leads, and the potentiometer box containing a cell, slide wire, and zero point galvanometer. The length of the drum-wound slide wire turned into the circuit is the measure of the matching current. Automatic potentiometers which are also generally recording, operated on various principles such as slide wire, photoelectricity, and a combination of the two, are in very general use.

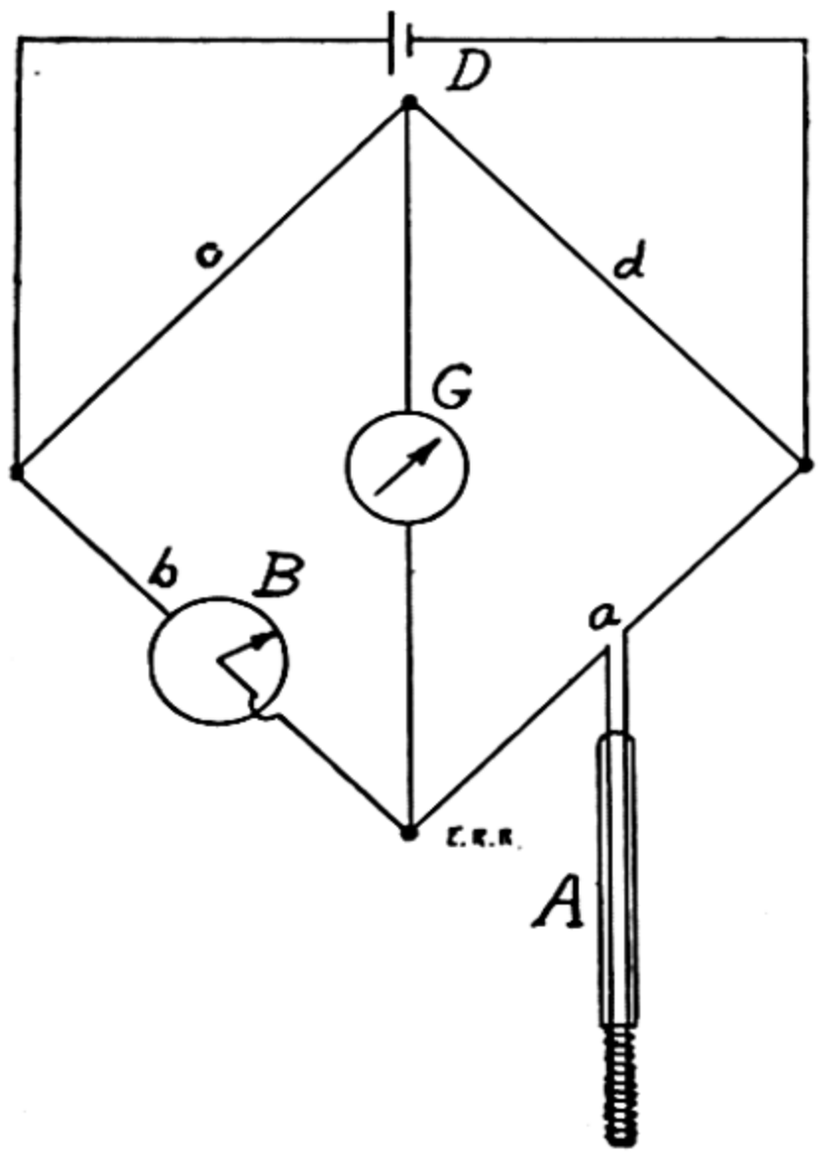


FIGURE 323.—The platinum resistance pyrometer. *A* is the fire-end, forming arm *a* of a Wheatstone bridge; *B* is the drum-wound slide-wire, forming arm *b*; *c* and *d* are the other two arms, which consist of fixed resistances; *G* is the zero galvanometer; *D* is the dry cell used for intermittent readings.

For precision work, in the laboratory, the cold junction which is here the binding post at the exit of the wires from the fire-end, is placed in an ice bath; in the plant, the temperature of the room is constant enough. The greater the difference in the temperatures of the two junctions, the less does it matter whether the room temperature is constant or varies somewhat; hence in this respect, high temperatures will be more accurately read.

The following pairs are suitable for the temperatures listed opposite them:

Copper-constantan	room temperature up to 500° C.
Silver-constantan	" " " " 700° C.
Iron-constantan	" " " " 1000° C.
Chromel-alumel	" " " " 1000° C.
Platinum-platinum+10% rhodium alloy	" " " " 1400° C.
" " "	for short periods to 1500° C.

Constantan [4] contains 60 per cent copper and 40 per cent nickel; chromel, 90 per cent nickel and 10 per cent copper; alumel, 98 per cent nickel and 2 per cent copper. The alloy platinum-iridium is also used instead of platinum-rhodium.

[4] So named because its electrical resistance is practically constant over a wide range of temperatures.

The relative sensitivity is indicated by the figures in the table below:

	E.m.f. in Millivolts	
	at 500° C.	at 1500° C.
Copper-constantan	27.8	...
Silver-constantan	27.6	...
Iron-constantan	26.7	...
Chromel-alumel	20.8	...
Platinum-platinum+rhodium alloy	4.4	15.1

Resistance Pyrometer. The resistance of a coil of platinum varies with the temperature; this property is the principle of the resistance pyrometer. The coil is made one of the four arms of a Wheatstone bridge; a slide-wire,

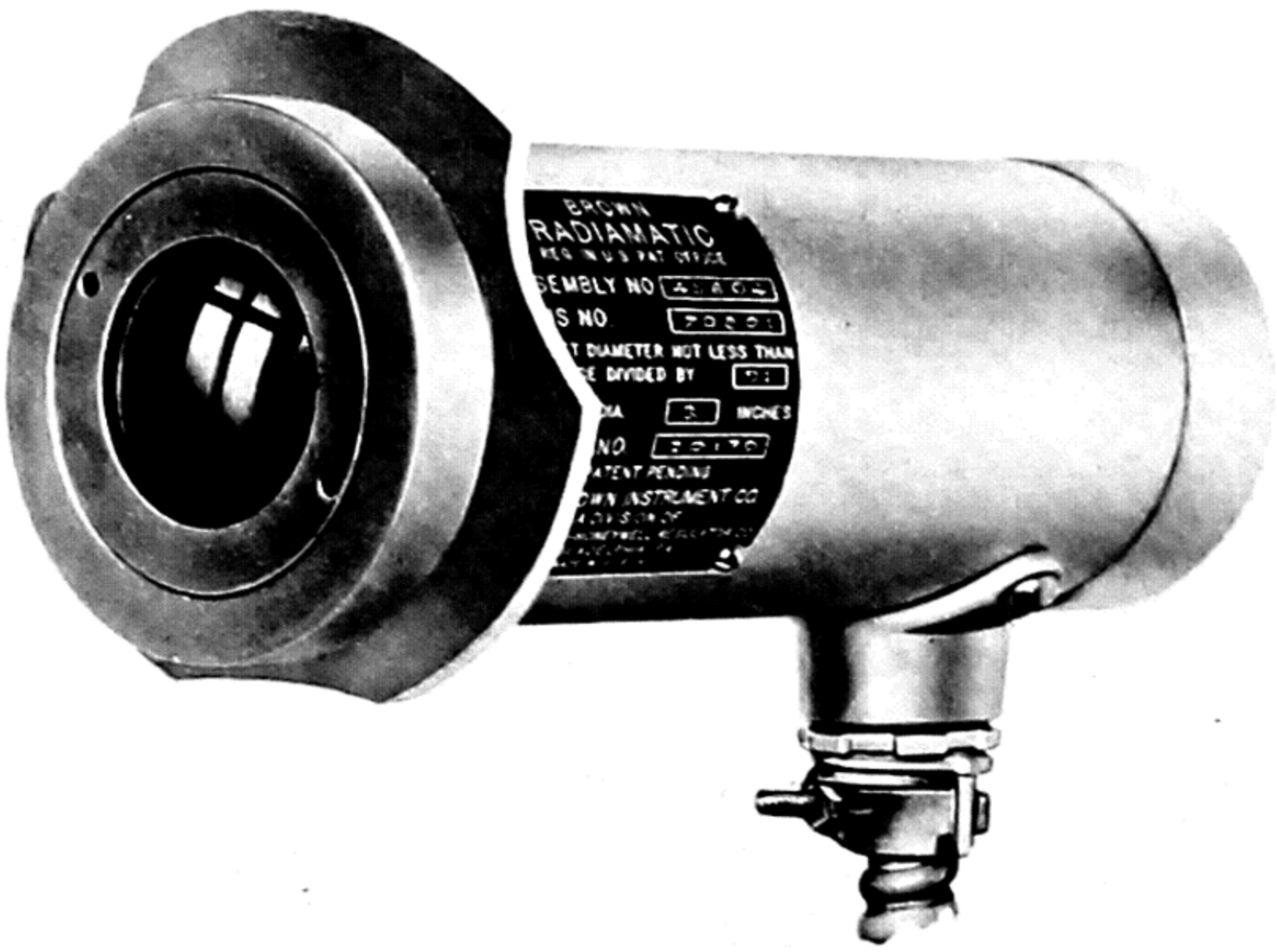


FIGURE 324.—The Radiamatic, an example of the radiation pyrometer, showing the collecting lens and conduit connections. (Courtesy Brown Instrument Company, Philadelphia, Pa.)

drum-wound, is adjusted so that the needle of a galvanometer shows no deflection; the length of wire needed for this adjustment is the measure of the temperature. The reading is direct, as the scale is graduated in degrees. The arrangement is shown in Figure 323.

The platinum resistance pyrometer is not as rugged as the thermocouple; it is also slower in response. If it is fixed in the region to be measured and not removed except for shutdowns, it is a reliable instrument and will give many years service. It is best suited for temperatures below 900° C.; for instance for the mechanical salt-cake furnaces, it has proved itself well adapted.

Radiation Pyrometer. The radiation pyrometer receives heat radiations from a furnace or hot body [5] through a collecting lens which focuses them

[5] A "black body" absorbs all incident radiations, transmits none, and itself radiates as fast as it absorbs.

on a very small thermopile. The current generated is measured by means of a potentiometer, hand operated or automatic. The cold junction is screened from heat radiations. The radiation tube may be held in the hand, or it may be mounted in a fixed position. The radiation pyrometer has been gaining over other instruments because none of its parts need to be inserted in the hot chamber, fluid or wall, with its attendant damage.

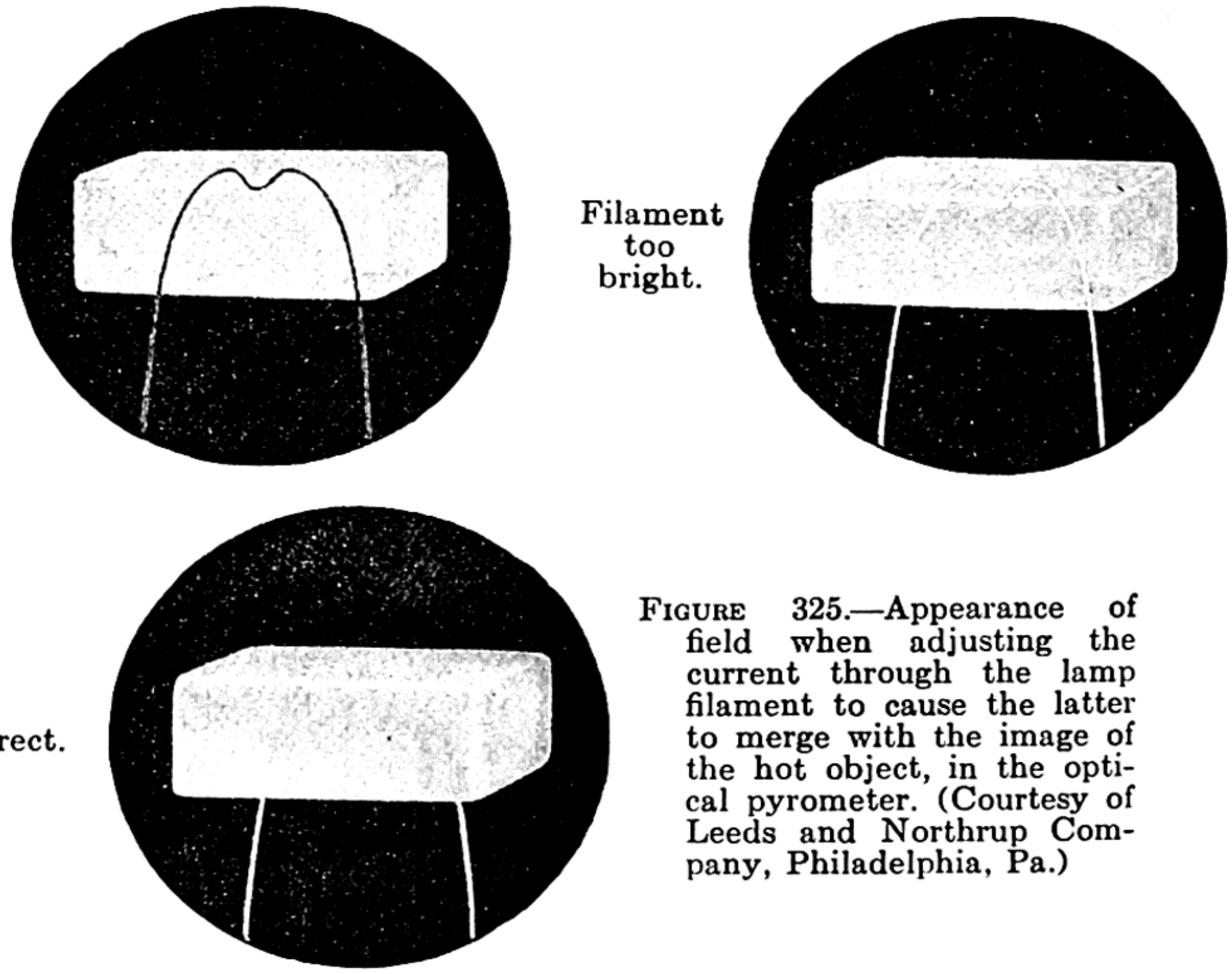


FIGURE 325.—Appearance of field when adjusting the current through the lamp filament to cause the latter to merge with the image of the hot object, in the optical pyrometer. (Courtesy of Leeds and Northrup Company, Philadelphia, Pa.)

The Radiamatic for intermediate range measures temperatures up to 2300° F. (1260° C.), and has a silica lens. The high-range Radiamatic measures temperatures between 2300 and 3200° F. (1760° C.) and higher, and has a "Pyrex" lens. The target diameter should not be less than one twentieth of the distance between the lens and the object.

Optical Pyrometer.[6] The optical pyrometer shares with the radiation pyrometer the great advantage of not requiring introduction into the bath or region to be measured. The inner wall of a window-glass melting pot, for instance, is sighted through the instrument; in the field of vision a platinum loop is placed. The loop may be heated to dull red, bright red, or white, by sending a varying quantity of current from a dry cell through it. Just so much current is sent through as needed for exact matching of the field, when the wire loop cannot be seen at all; a little more current and the loop appears, and is whiter than the field; a little less and it appears again, but darker than the field. The reading for a perfect match is readily duplicated by different observers to within 4° C. near 1400° C.

[6] Optical pyrometers are radiation pyrometers limited to visible radiations.

The complete apparatus consists of the sighting tube containing the filament lamp, a storage battery, a rheostat, and a milliammeter. Its field of usefulness lies from temperatures corresponding to dull red, about 600° C., to temperatures higher than correspond to white heat.

Instruments procured from the dealers are ready for use, and are usually put into service without further testing. Should any doubt arise as to the correctness of the reading, the instrument may be sent to the Bureau of Standards at Washington, for certification. The standardization may be done in the laboratory of the plant if enough time is allowed to acquire the necessary technique, for it is specialized work, and very misleading figures may be obtained. The fixed points recommended are:

Melting point	of	Zinc	.....	419° C.
"	"	"	Aluminum	657
"	"	"	Silver	961
"	"	"	Gold	1063
"	"	"	Nickel	1452
"	"	"	Palladium	1549

The most reliable method of testing a thermocouple for the gold melting point for instance, would be to separate the wires at the fire-end junction (hot junction) and place a short piece of gold wire between them making good electrical contact; the rest of the apparatus would be as usual. On heating the fire-end slowly at a definite rate and watching the millivoltmeter, there will occur an interruption to the gradual rise of the needle and a sudden return to zero; the maximum reading made will correspond to the melting point of the gold. At least two such points are tested and the curve drawn for the intermediate temperatures.

The comparison of two different pyrometers is another way to standardize; for instance, a radiation pyrometer may be sighted on the fire-end of a platinum-platinum rhodium thermocouple; or two thermocouples may be placed side by side. Sufficient time must be allowed for both instruments to reach their maximum reading, and the means of three trials is taken.

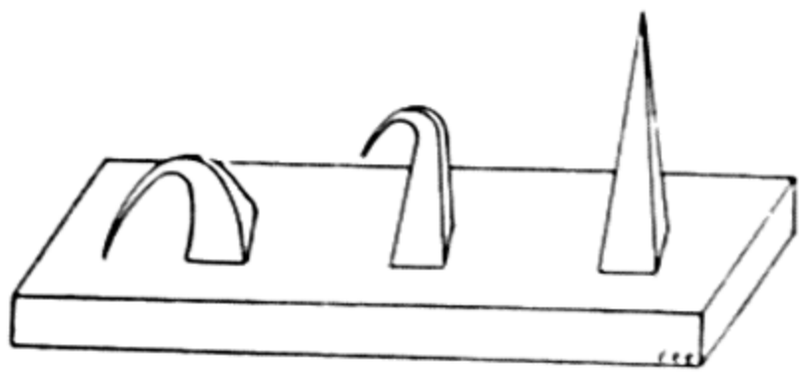


FIGURE 326.—Pyrometric cones.

Pyrometric Cones. Pyrometric cones, formerly called Seger cones, are really slender triangular pyramids and are made of mixtures of clays with definite fusion points. (*See* Figure 326.) They are used in groups of three, numbered for instance 9, 10, and 11, set close together in a small lump of clay; the group is pushed into a porcelain kiln, as example, within range of a peephole. The firing will be increased until No. 9 melts and bends over completely, No. 10 softens enough to have its tip leaning over; No. 11 is still erect. If the firing is now maintained constant, or decreased, so that No. 11 remains unaffected, the maximum temperature which has been reached is

that corresponding to No. 10, namely, 1305° C.; that corresponding to No. 9 has been exceeded, 1285° C., while that temperature corresponding to No. 11 has not been reached, 1325° C. It may be said that the temperature reached is determined to within 20° C.; this is not quite certain, but the observation of the cone may be made finer in this way: It is observed that the upper half of the cone leans over, the lower half is erect; that point is taken to be exactly 1305° C.; if only the upper third leans over, the temperature is about 1295° C.; if the lower half has started to lean over, the temperature is about 1315° C.; hence the accuracy may easily be said to be within 10° C. By making intermediate cones, the limit may be narrowed to 5° C. and less; the commercially obtained cones are made for 10° to 20° C. intervals, as that is close enough for ordinary operation in many industries. They are inexpensive, which is essential, as they are used but once.

For the range 1160° to 1810° C. Nos. 1 to 36 are made, leaving a difference of 10° to 20° between any two; the materials are feldspar, marble, quartz, and kaolin in varying proportions; No. 1 has 83 per cent feldspar, and only a trace of kaolin; whereas No. 36 has no feldspar, and all kaolin. The most widely used cones are Nos. 1 to 12, 1160° C. to 1335° C. Another series of ten numbers registers over a range of 895° C. to 1145° C.; and still another between 605° to 875° C. (Chapter 10).

Potteries are the plants in which pyrometric cones were chiefly in use; they still are, but of late the recording thermocouple pyrometer has been introduced. The cones will continue in use, however, where the accuracy of the temperature indication which they give is sufficient for the control of the operation. If a fluctuation of 20° C. does not matter, it is a waste of effort to make measurements within 4° C. The pyrometric cones suffer as all indicating instruments do, from the fact that they do not give information on how long a certain temperature was maintained; this is done only by the recording pyrometers.

Thermal Conductivity Cell for Gases. Supplementing chemical methods [7] for gas analysis, the thermal conductivity of gases has been made the basis of a method of analysis [8]; heat enters the gas through platinum spirals which receive a measured current. The heat conductivity values which follow will indicate the applicability of the cell:

Air	1.00	Ammonia	0.81
Hydrogen	7.35	Methanol gas	1.31
Carbon dioxide	0.58	Nitrogen	1.00
Sulfur dioxide	0.41	Oxygen	1.00

The cell for thermal analysis of carbon dioxide containing gases as manufactured by the Brown Instrument Company, may be taken as an example. Two gas wells are provided, through one of which (*O* in Figure 253), a portion of the gas to be analyzed is continuously bled, while the other (*P*) contains the comparison gas, air. In each cell there are 4 filaments (one

[7] As to analysis of gases, read "New forms of gas analysis apparatus," G. A. Burrell, *Ind. Eng. Chem.*, 4, 297 (1912). The simple Orsat apparatus is described in Chapter 12.

[8] "Electrical gas analysis for continuous processing," A. C. Schmid, *Chem. Met. Eng.*, 36, 230 (1929).

is not shown in figure); each pair forms one arm of a Wheatstone bridge, hence two arms per cell, four arms for the two cells. A given current is passed through all filaments, heating them. Depending upon the thermal conductivity of the gas, heat leaks out to the metallic enclosing pipe, more or less fast. In the case of CO_2, it leaks out less fast than for air. As a

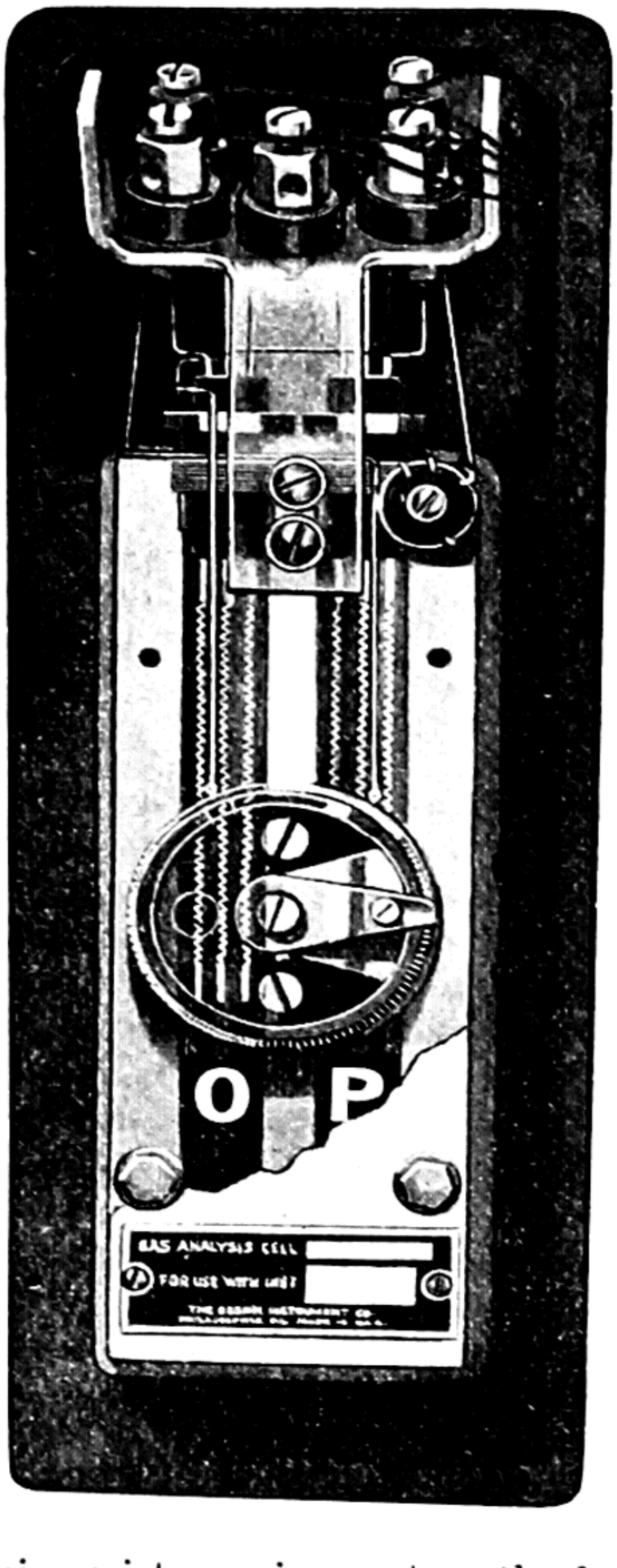


FIGURE 327.—Cell for thermal-electric analysis of a gas containing carbon dioxide; see text. (Courtesy of the Brown Instrument Company, Philadelphia, Pa.)

result, the filaments in *O* are hotter, their resistance is greater; the bridge is unbalanced. A different current is then able to flow, and this actuates indicating and recording devices. A change in the composition of the gas is recorded in less than a minute.

In the "*Ranarex*" *analyzer*, which depends upon the density of the gases for its action, there are two chambers, each with a driven impeller which drives the gas forward; and each with a fan wheel which receives the driven

gas. Suitable outlets are provided for the gases. The impeller in chamber A runs clockwise. The fan wheel tends to rotate in obedience to the impulse from the gas. It cannot rotate, however, because it is connected by an outside rod to the fan wheel in the lower chamber; here, the arrangement is the same, but the direction of the driven impeller is counter-clockwise; hence, the impulse on the wheel in chamber B is opposite to that in A. The same belt drives the two impellers. The rod which connects them registers the differential torque of the two fan wheels. If the gas in A is of the same density as that in B, the torque on wheel A will be equal and opposite the torque on wheel B, for the velocity given the gases are the same, and their densities do not differ. If the density of the gases differ, the torque differs, and there will be a movement of the rod toward one of them, away from the neutral position. This movement is magnified by means of levers and is transferred to a needle which travels over a scale.

The "Ranarex" was devised primarily for flue gas analyses; the density of carbon dioxide is very different from that of air (as 44 is to 28.8) and a small percentage, more or less, has an effect on the torque of the wheels, one running on air. For ammonia-air mixture, it has been equally successful; here again the difference in densities is considerable (as 17 is to 28.8). For ammonia, the chambers are kept dehydrated by sulfuric acid; for flue gas, they are kept hydrated by water.[8a]

Air Conditioning

In many industries, such as paper, textiles, printing, it is necessary to regulate the amount of moisture contained in the air of the factory rooms, for only by maintaining a certain humidity, at a given temperature, can the moisture-susceptible properties of the products be controlled. The "relative humidity" of the air is the ratio of water vapor actually contained in it to the maximum amount it may contain at that temperature. This latter would be saturated air, whose relative humidity would be 100. It is important that the temperature at which a particular relative humidity is to be provided, be stated, for the same relative humidity at different temperatures stands for different absolute amounts of moisture. Thus, 40 relative humidity at 65° F. corresponds to 36 grains of moisture per pound of dry air, but 40 relative humidity at 85° F. corresponds to 72 grains of moisture, per pound of air.

The relative humidity is determined by means of two thermometers tied together; one thermometer bulb is left dry, the other is fitted with a wet cloth over its bulb. On placing these two thermometers, now termed a psychrometer, in the air to be tested, the wet bulb thermometer will register a lower temperature than the dry one. The differential will be greater the drier the air. From the temperatures, the relative humidity is read off on the chart (*see* Figure 328), and applies to air at the temperature of the dry bulb thermometer. The absolute amount of moisture in grains, per pound of dry air, may also be found by means of the chart. With a sling psychrometer, the necessary equilibrium is attained in a minute.

[8a] The Permutit Company, New York.

Air conditioning means providing air with a definite, predetermined amount of water vapor, at a stated temperature. Partial humidification means the injection of atomized air in the rooms, in order to raise the moisture content. Complete humidification means either lowering, or raising of the moisture content, as may be necessary. For the latter, as a rule, outside air is passed through a spray of circulated (and cooled) water at a low

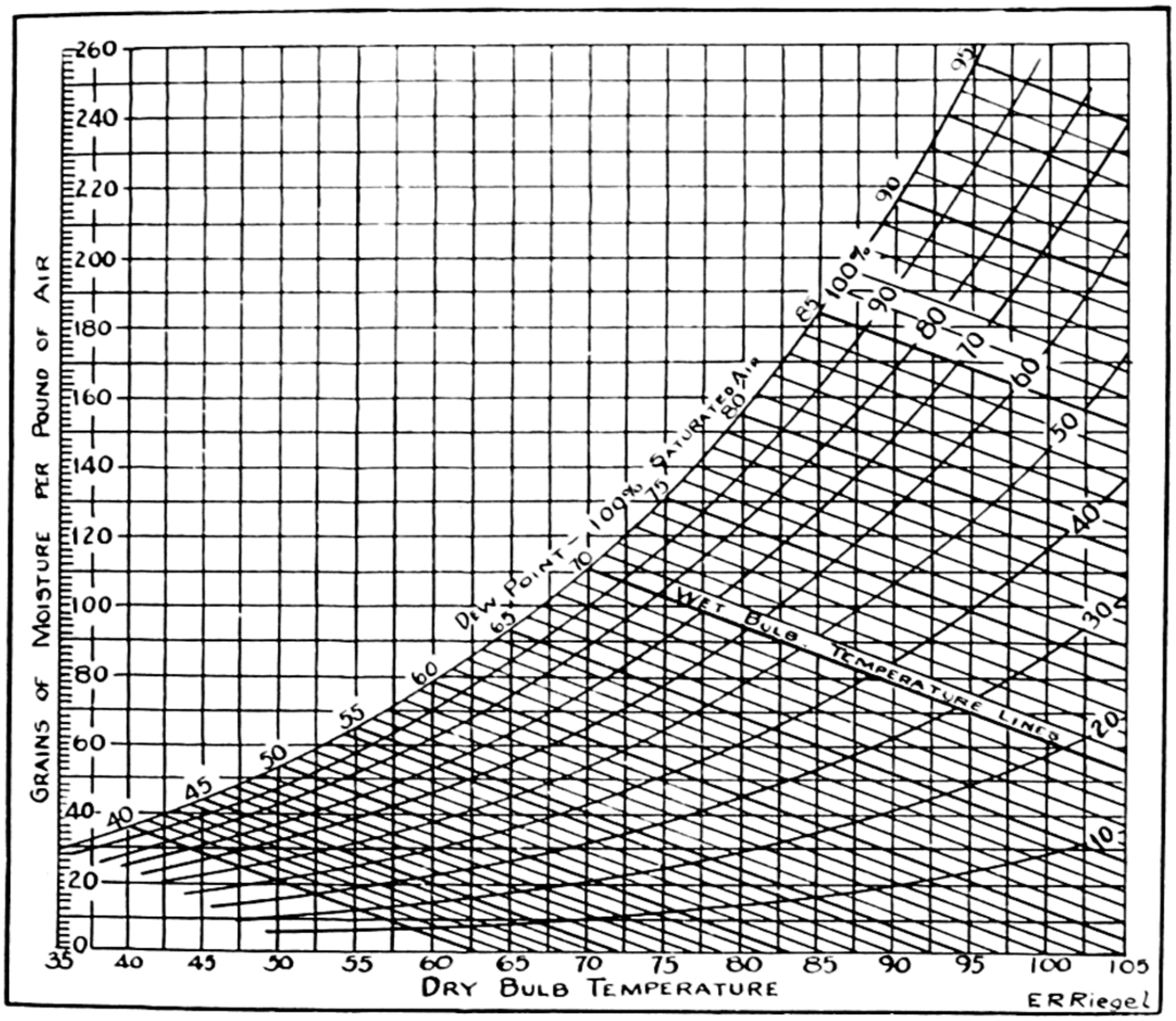


FIGURE 328.—Psychrometric chart, for determining the absolute and relative humidity in the air from wet and dry bulb thermometer readings. The curved lines are the relative humidities.

temperature; the air becomes saturated with moisture at the temperature of the spray. This may involve a cooling, and a deposition of water (dehumidification). Next the air passes baffles in order to deposit entrained droplets, and finally over steam coils in order to raise it to the temperature prescribed. There are many variations in procedure. In all, a fan pulls in the new air, and delivers it to the ducts leading to the various rooms. Refrigeration and silica gel have been used for dehumidification.

The Cottrell electrical precipitator (described in Chapter 43) has been applied to air conditioning. Its special efficacy is the removal of suspended

solid particles below 5 microns in diameter, which are frequently of bacterial nature, and which escape the ordinary dry filter. The Westinghouse Electric and Manufacturing Company has announced (March 1937) a commercial Cottrell unit suitable for the home. The unit will follow the dry filter. The charged particles will pass between plates with a voltage gradient of about 1400 volts per inch. All danger of ozone or nitric oxide formation is avoided by lowering the voltage to 15,000 from the original 60,000.

Measurement of the Flow of Gases and Liquids

The measurement of the flow of a gas or a liquid is a frequent operation; the quantity of a waste gas, sent up a chimney for instance, may be sought because of a certain content of a valuable gas or vapor; if the volume of gas passing out is known, an analysis giving the percentage by volume of the valuable gas is all that is needed to make the calculation as to how much is lost per day.

The Pitot tube and the Venturi tube both measure velocity per second, and this multiplied by the area of the pipe gives cubic feet per second.

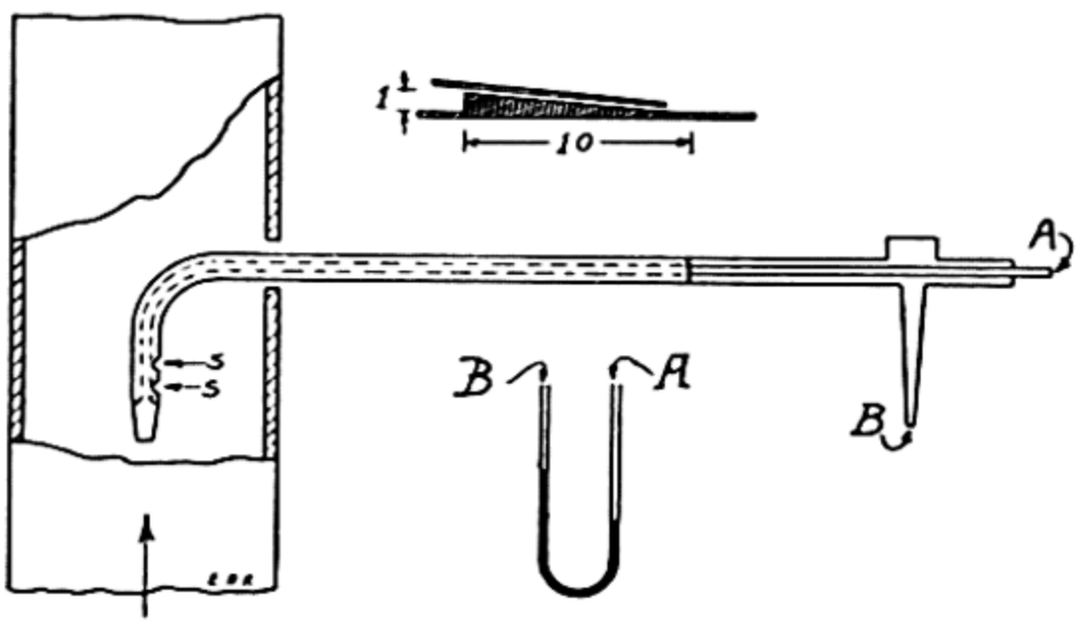


FIGURE 329.—A brass Pitot tube. *A* and *B* are connected to a vertical *U*-tube as indicated; for low velocities, the inclined manometer shown here is used.

An occasional measurement for which no installation has been provided is made by means of the Pitot tube; the Venturi tube is built into the line, and all the gas passes through it at all times.

Gas flow meters for small rates of flow may be constructed in the laboratory, and of glass.[9]

The Pitot Tube. The Pitot tube is a double tube, as indicated in Figure 329. One opening, facing upstream, receives velocity head and static head [10] combined; a rubber tube transfers this double pressure to one leg of a *U*-tube. Two small pin-hole openings permit the static pressure to pass through the outer chamber through a rubber connection to the other leg of the U-tube. In this way, the static pressure is eliminated in the reading; the difference in levels in the two legs of the *U*-tube is due to velocity pressure alone. The *U*-tube is filled with ether, or thin oil, or some other chosen liquid; for low velocities, the lightest liquid is used, ether, in order to obtain as large a reading as possible. The accuracy of the reading is increased by ten by inclining the *U*-tube to near horizontal position, on slope of 10 to 1;

[9] *Ind. Eng. Chem.*, 11, 623 (1919).
[10] The static head is the absolute pressure in the pipe.

this form is known as the Swan manometer. With the height expressed in terms of a vertical column of water, the formula $v = \sqrt{2gh}$ is used, usually with a factor of 0.9 to allow for the dragging effect of the pipe walls.

Venturi Tube. If the normal diameter of a pipe be narrowed to form a throat, then flared out again to the original size, another means is provided to measure velocity. The relation between the diameters and the length of the constricted portions is approximately as indicated in Figure 330. The pressure at the throat will be lower than in the full-sized

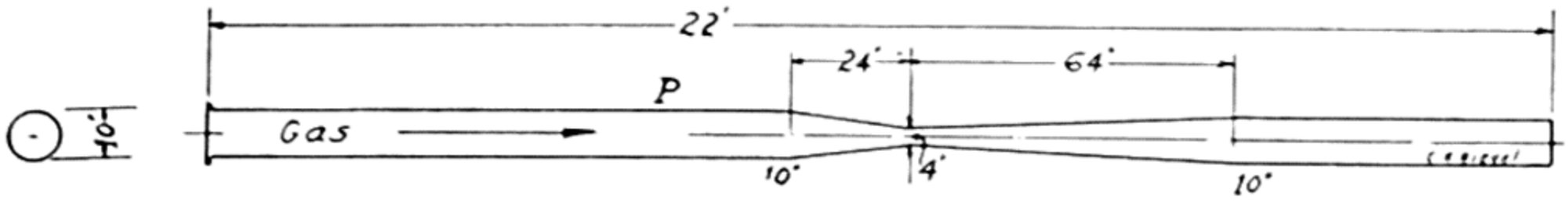


FIGURE 330.—The Venturi tube for measuring the flow of gases; a small pipe is soldered to the 4-inch throat, another at *P*, and connected to a *U*-tube.

pipe, if a gas is traveling through, and the difference between the two pressures, measured on a *U*-tube as before, is proportional to the velocity. In chemical plants, it is customary to standardize each Venturi tube by sending known volumes of air at various temperatures through it, and recording the readings. The theory is essentially the same as for the Pitot tube.

The Venturi tube may be vertical or horizontal, of lead or cast iron; the liquid in the *U*-tube is usually water, sometimes concentrated sulfuric acid, rarely mercury.

In the Thomas meter, for gases, essentially an electrical thermometer, a measured quantity of heat is furnished a traveling gas at a given point in the conduit; the increase in the temperature of the gas is inversely proportional to the quantity passing through per second; the more gas passes, the smaller the rise in temperature. A modern form of this valuable device is illustrated in Chapter 14.

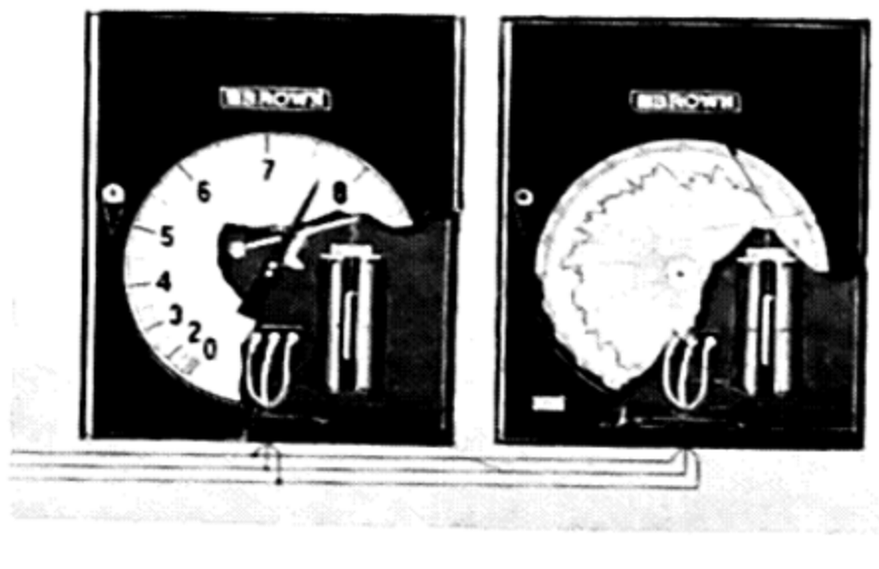


FIGURE 331.—An orifice electric flow meter, indicating and recording. (Courtesy of the Brown Instrument Company, Philadelphia, Pa.)

In an *orifice flow meter*, a disk with a central opening, the orifice, is inserted in a pipe, constricting the flow of gas or liquid, and creating a differential in pressure. The pressure is higher upstream. The differential is applied to a mercury manometer, and its changes in level are read by means of a float, or electrically. In the Brown Electric Flow Meter, the changes in

level of the mercury on the low pressure side cause a stainless steel float carrying a magnetic armature on a non-metallic nickel-chromium rod to move up and down. The steam and float are enclosed in a non-magnetic ferrous alloy tube. Over the outside of this tube a divided inductance coil fits. Auxiliary electrical apparatus passes more or less current, as the divided inductance coil is affected more or less by the magnetic armature within the closed tube. The auxiliary apparatus includes indicating and recording devices.

The metering of fluids by means of a *rotameter* is widely done in the industries. Corrosive as well as non-corrosive liquids and gases are handled

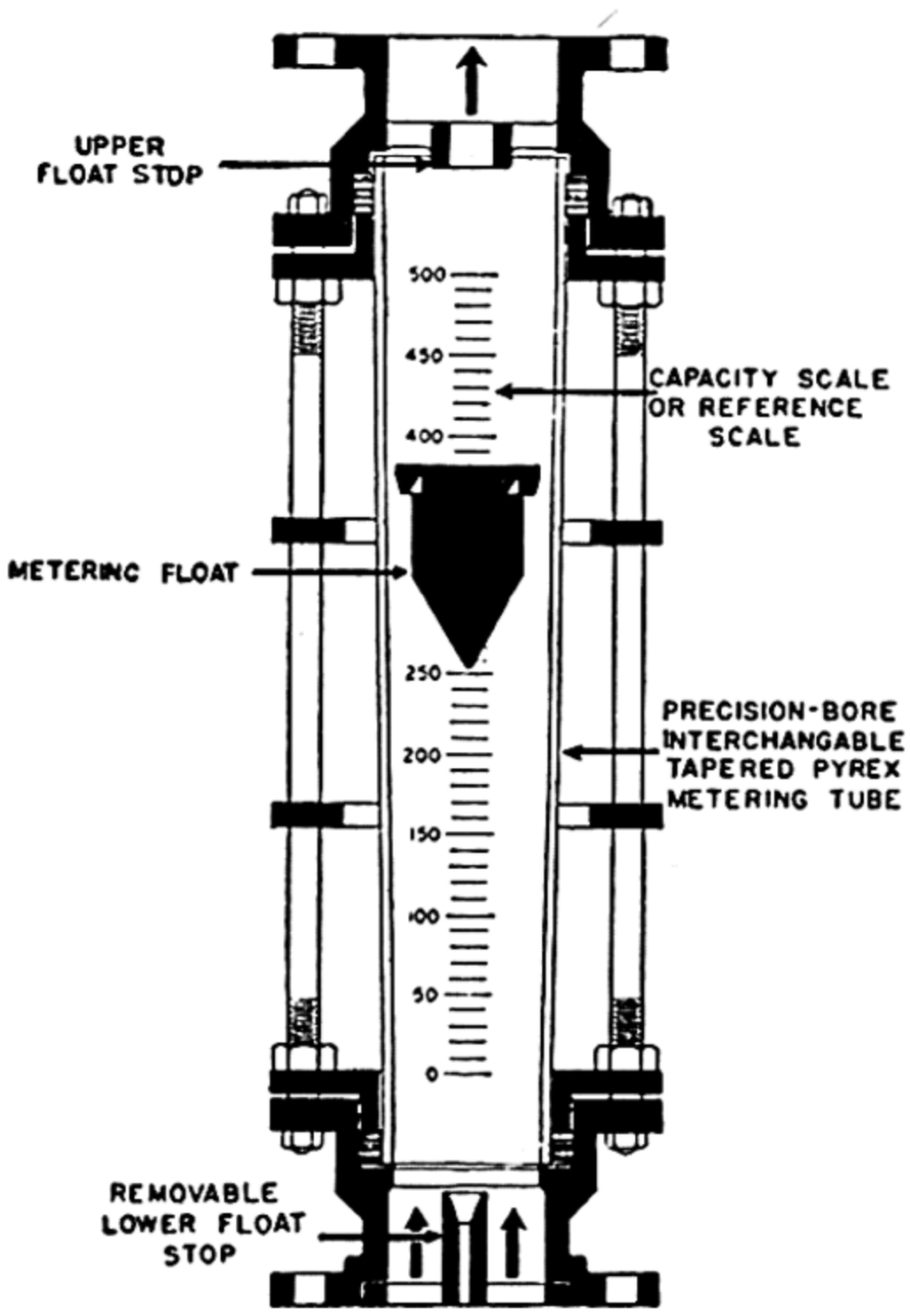


FIGURE 332.—The fundamental design of the rotameter for measuring the flow of liquids and gases. The float assumes a position in the tapered tube which corresponds to the volume passed. The direction of flow is shown by the arrows. The rotameter is an orifice meter with variable area. (Courtesy of Fischer and Porter, Hatboro, Pennsylvania.)

successfully; transparent and light-colored liquids present no difficulty; more startling is a development which permits with equal ease the metering of opaque fluids and slurries. This instrument originally depends upon the sighting of the float. Opaque fluids and slurries are handled by means of a float with a rod-extension upward; the top of the rod moves in an upper chamber in which there is no flow. Its position indicates the flow.

The applications away from standard metering which deserve special mention are, for example: the use of a rotameter for measuring accurately the air which is incorporated into the cream for ice-cream before freezing it; the manufacture of sponge rubber, in which rotameters measure a given quantity of air to be incorporated into the latex, instead of merely whipping it up.

The numerous water meters of varying construction are reliable and useful volumetric meters, for all kinds of liquids as well as for water.

Electrometric Methods in Plant Operation

In a number of industries, the control of the acidity, or in more general terms, of the concentration of hydrogen ions, is of great importance for uniform production. A number of devices for the electrometric determination of this value have been successfully introduced.[11] The development of such methods for laboratory use, that is, chiefly analysis,[12] had to precede, and this has been in progress for the last fifteen years or so. Two main divisions may be observed.

The first is a conductivity group, in which a measurement depends upon the conductivity of a solution to the electrical current, whether that conductivity be due to acidity, alkalinity, or to salts. If it is known that salts are absent, and that only one certain acid can be the cause of the conductivity, this method can be used for the control of acidity.

The second group is the potentiometric group, applied chiefly to the determination of hydrogen-ion concentration in a solution. Its superiority over any other method lies in the fact that it is applicable even in the presence of salts, and to colored solutions which would prevent the use of indicators. The method rests upon the measurement of the potential of a primary [13] cell made up of two halves, one the hydrogen half, the other the calomel half, a saturated solution of calomel in contact with a potassium chloride solution. Such a cell generates a small current of a definite potential (voltage) if the solution in which the hydrogen electrode rests is normal. The calomel half-cell remains constant. By hydrogen electrode is meant a platinized platinum rod or plate over which bubbles of hydrogen pass at the rate of three a second, or similar rates. If the concentration of the acid solution is varied, the potential of this composite cell will also vary, and the variation will be directly proportional to the change in concentration. Hence this provides a means of following changes in the concentration of the hydrogen ions; with the addition of electrically controlled mechanisms, correcting solutions may automatically be introduced. The potential is measured by matching it with a second potential in the opposite direction from an outside source, lowered or raised by the introduction or removal of resistance, until a galvanometer between the two circuits indicates no flow. The amount of the resistance introduced or removed is the real measure of the potential change.

The industrial cell may employ the hydrogen electrode, or this may be replaced by the tungsten or pyrolusite electrode or other non-gas electrodes. A rugged cell entirely protected by a phenol formaldehyde plastic sleeve, with all the necessary apparatus transportable, is described in the literature.[14]

[11] "Progress of electrometric control methods in industry," Henry C. Parker, *Ind. Eng. Chem.*, **19**, 660 (1927).

[12] Consult "The determination of hydrogen ions," Wm. M. Clark, published 1928 by Williams and Wilkins Co., Baltimore; also the chapter on "Electrometric methods in analytical chemistry," by N. H. Furman, pages 823-863 in Vol. 2 of "Treatise on physical chemistry," H. S. Taylor, New York, D. Van Nostrand Co., 1925.

[13] That is, "current-producing cell," in distinction from the electrolytic or "current-consuming cell."

[14] *Ind. Eng. Chem.*, **17**, 639 and 737 (1925).

The electrometric methods of the first class, depending on conductivity, and measured and applied to control by means of a Wheatstone bridge with auxiliary apparatus, serve to detect leakage in surface condensers in power plants. The condensed water is pure and does not conduct the current, but if any cooling water enters through a newly developed hole, let us say it is sea water, the contaminated condensed water will at once allow the current to pass; by means of auxiliary mechanism, a red light will appear announcing the leak.

Control by means of the measurement of the potential due to hydrogen-ion concentration has been applied to the automatic addition of caustic soda and sodium phosphate to boiler feed water which is acid, to maintain the proper acidity in a neutralizing bath for alkali cotton, and to several other industrial problems.[15] Temperature must always be taken into consideration.

A recent development for the rapid determination of carbon in a molten steel while it is in the furnace, open hearth or electric, is the *Carbometer*,[15a] a Swedish instrument which utilizes the degree of magnetic induction which can be imparted to a test sample of steel; the magnetic induction varies with the carbon content. A $\frac{3}{8}$-inch rod is cast from the spoon sample, quenched, and placed in one of two funnel-shaped vertical receivers in the carbometer; one slot is for hardened steel (over 0.40 per cent C.), the other for unhardened steel. Turning a knob starts the clockwork which drives an armature; the test piece is magnetized. When the armature stops rotating (clicks), pressing a button allows the final rotation of the armature from the highest magnetic field strength position, through 90°, to the lower field strength, inducing a current of electricity in the coil surrounding the test sample. This current is measured on a ballistic galvanometer, shunted in automatically when the armature reaches its final position. The needle reading is translated into carbon percentages by means of a chart, read to within 1 point (0.01 per cent C.). Charts are made at the plant for the types of steel manufactured, inasmuch as other metals alter the magnetic induction. The readings are checked against laboratory analyses.

The refractometer is a useful instrument of control. For example, in the process of hardening vegetable and animal oils to fats, the progress of the hydrogenation may be followed by the change in refractive index. A few drops on the split prism of an Abbé refractometer, with water circulation to give a definite temperature, permit a reading in a few seconds.

An automatic sampling device, for sampling wood chips, or any material from a spout, to a conveyor for example, has been described.[16]

Unit Operations and Unit Processes. In 1915, Dr. Arthur D. Little observed that "any chemical process may be resolved into a co-ordinate series of unit operations, as pulverizing, drying, roasting, crystallizing, filtering, evaporation, electrolyzing, and others." This suggestion has become part of the system of chemical engineering study. A recent addition to the

[15] *Ind. Eng. Chem.*, 19, 660 (1927).

[15a] Carbometer, patent of Malmberg-Holström, manufactured by Aktiebolaget Alpha. Sundbykerg (near Stockholm), Sweden.

[16] *Chem. Met. Eng.*, 37, 350 (1930).

already long list is diffusion.[17] Other unit operations are agitation and mixing, fractional distillation. The process of making caustic soda by causticizing soda ash with lime is divided into four unit operations: lime slaking, causticizing, caustic liquor decantation, lime mud washing. To the unit operations there have been added the chemical engineering unit processes, to the great advantage of the development of the science of chemical engineering.[18]

Other Patents

U. S. Patent 2,020,588, fluid flowmeter; 2,021,615, liquid level indicator; 2,012,616, method and apparatus for introducing reagents into liquid suspensions; 2,022,695, controlling flow of volumes of liquids; on pyrometers and thermocouples, 1,890,701; 1,808,507; 1,820,219, optical; 1,825,229, and 1,788,849, same; 1,845,271, thermocouple; 1,849,832, thermocouple for high temperatures, with a carbon and a tungsten element; 1,823,706, same, but tantalum carbide and graphite elements.

Problems

1. The outside air is 40° F. and 30 relative humidity. This air is moved into the building, gradually warming to 76° F., with no gain or loss of water. What is the relative humidity for such air in the building, and what would the psychrometer readings be?

Answer: 9 relative humidity; 76° F. dry bulb; 49° F. wet bulb.

2. Starting with any air, how would you furnish a room with air at 72° F. and 50 relative humidity?

Answer: Cool or warm to 51.5° F. and saturate with H_2O at that temperature, then warm to 72° F.

3. A sling psychrometer gives readings: wet bulb, 60° F.; dry bulb, 78° F. What is the relative humidity? This air is completely dessicated and then warmed to 78° F. again. What is its relative humidity, and what are the wet and dry bulb readings?

4. For a comparison of heat effects, the following purely theoretical comparison should be made: Air at 80° F. and relative humidity 80, at the rate of 10,000 cu. ft. per minute, passes over a water surface; it takes up more moisture until saturated. How much water in pounds per pound of air are taken up, and how many B.t.u. does their vaporization represent?

To cool this air to 55° F. means the removal of how many B.t.u., equivalent to the vaporization of how many pounds of water? If the heat consumed in the vaporization in the first part of the problem is not sufficient, how many pounds of water at 55° F. will be required to remove the remaining B.t.u. by contact, without vapor exchange?

Take the mean specific heat of the air as is over the range specified as being 0.01826 B.t.u. per cu. ft., and the heat of vaporization for 1 pound of water over the same range as 1060 B.t.u.: take 1 cu. ft. of the air as is to weigh 0.0761 pound.

5. In reality, when 80° F. air with 80 relative humidity is cooled slightly, the temperature will drop to wet bulb temperature, the loss of sensible heat being equal to the gain in latent heat of water vaporized. The latent heat is the heat obtainable when water as gas becomes liquid water. What is the wet bulb temperature which goes with our original datum?

A pound of air at a dry-bulb temperature of 80° F. and a wet-bulb temperature of 75° F. contains 124 grains of water. When such air passes through a spray of water at the same temperature, water will be taken up. The dry-bulb temperature will fall, but the wet-bulb temperature will remain 75° F., and the dry-bulb temperature will equal it. The dew point, which is originally 73° F., will gradually rise to 75° F., when saturation is realized. How many grains of water will it contain now, and what is the gain?

[17] Symposium on diffusion as a basis of Unit Operations, *Ind. Eng. Chem.*, 33, 424 (1941).

[18] "A plea for the Unit processes," by D. B. Keyes, *Chem. Met. Eng.*, 41, 244 (1934).

At ordinary temperature, 1 grain of water absorbed means a lowering of about 8.5° F. in the dry-bulb temperature.

6. An air-conditioned system delivers to the space to be conditioned 20,000 cu. ft. of air per minute at 65° F. dry bulb and 40 per cent relative humidity. Of this air, 75 per cent is being recirculated. Determine the refrigeration effect, in tons, required when the outside air has 90° F. dry bulb, and 77° F. wet bulb, the return air has 75° F. wet bulb, and relative humidity of 34 per cent, and the total 20,000 cu. ft. passes through a saturating air washer. Assume 13.6 cu. ft. of air per pound.

NOTE: The standard refrigeration ton is 200 Btu./minute, or 12,000 Btu./hour or 288,000 Btu./day. The value per day is the one generally used. A complete psychrometric chart may be obtained from any firm which manufactures blowers or air conditioning equipment. For example, address the Buffalo Forge Company, Buffalo, N. Y.

READING REFERENCES

"Mechanical engineers' handbook, Lionel S. Marks, New York, McGraw-Hill Book Co., 1942.

"The photo-electric cell in chemical technology," A. J. McMaster, *Ind. Eng. Chem.*, 22, 1070 (1930).

"Handbook of Industrial Temperature and Humidity Measurement and Control," M. F. Behar, New York, Instruments Publishing Co., 1932.

"High temperature control: photoelectric-tube pyrometry," Lewis R. Koller, *Ind. Eng. Chem.*, 23, 1379 (1931), applied to control of industrial furnace to temperatures of from 1000° C. (1832° F.) upwards.

"Rise of air conditioning, with particular reference to the chemical field," W. L. Fleisher, *Ind. Eng. Chem.*, 23, 732 (1931).

"Air-conditioning in the drug-manufacturing industry," William A. Hanley, *Ind. Eng. Chem.*, 25, 9 (1933).

"Air-conditioning for railway passenger cars," H. K. Williams, *Ind. Eng. Chem.*, 25, 13 (1933).

"New humidity chart simplifies combustion problems," Sirozi Hatta, *Chem. Met. Eng.*, 37, 165 (1930).

"American Society of Heating and Ventilating Engineers' Guide," New York, American Society of Heating and Ventilating Engineers, 51 Madison Ave., 1932, for information on air-conditioning.

"Bacterial control in air conditioning," T. S. Carswell, J. A. Doubly and H. K. Nason, *Ind. Eng. Chem.*, 29, 85 (1937).

"Absorption and Extraction," Thomas K. Sherwood, New York, McGraw-Hill Book Co., 1937.

"New carbometer control speeds production and improves quality," Gilbert Soler, *Metal Progress*, 31, 159 (1937).

"Automatic detection and control of hydrogen sulfide," S. Roberts and G. Minors, *J. Soc. Chem. Ind.*, 53, 526 (1934).

Unit processes symposium, *Ind. Eng. Chem.*, 36, 412-417 (1944).

"Temperature, Its Measurement and Control in Science and Industry," American Institute of Physics, New York, Reinhold Publishing Corp., 1941.

"Measurement of the flow of liquids and gases," E. Ower, *Trans. Institution Chem. Eng. (London)*, 18, 87-104 (1940).

"Instrumental methods of chemical analysis," Ralph Holcombe Müller, *Ind. Eng. Chem.*, Analytical Edition, 13, 667 (1941).

"Unit operations review," *Ind. Eng. Chem.*, 39, p. 3-42 (1947), now an annual feature.

"Silicones as new engineering materials," W. R. Collins, *Trans. Am. Inst. Chem. Eng.*, 42, 455 (1946).

"Chemical Engineering application for plastics," T. S. Carswell and R. U. Haslanger, *Trans. Am. Inst. Chem. Eng.*, 39, 755 (1943).

"Economic interrelationships of certain unit processes," R. H. Ewell, *Chem. Eng. News*, 25, 502 (1947).

"Design and development of apparatus for measurement of steam quality by electrical conductivity methods," by S. D. Powell, H. E. Bacon, Jr., I. G. McChesney and F. Henry, *Trans. Am. Inst. Chem. Eng.*, 33, 116 (1937).

"Applications of unit operations and processes in the ceramic industries," W. A. Koehler, *Trans. Am. Inst. Chem. Eng.*, 40, 575 (1944).

"A case study in package selection," H. C. E. Johnson, *Chem. Ind.*, 62, 394 (1948).

"Shipping equipment matches chemical industry pace," F. G. Moore and J. E. Weaver, *Chem. Ind.*, 63, 772 (1948).

"Fibrous silica, a new engineering material," L. Parker and J. J. Foster, *Chem. Eng. Prog.*, 44, 937 (1948).

"Materials of construction for chemical engineering," J. McKillop, *Trans. Inst. Chem. Eng.* (*British*), 13, 63-76 (1935).

"Applications of super-refractories made from electric furnace products," C. F. Geiger, A. A. Turner and O. R. Stach, *Chem. Eng. Prog.*, 44, 933 (1948).

"Polythene for the chemical plant," *Industrial Chemist (London)*, 25, 25 (1949).

Of the long list of metallurgical products, the production of pig iron and steel exceeds many times that of any other metal. Some of the newer products have received much advertising, necessary because of their newness, but tending to produce a wrong conception of their relative importance. Pig iron and steel are the giants, in war time as well as in peace time, except that in war time they are super-giants.

Chapter 47

Pig Iron

The manufacture of pig iron is on an enormous scale, as the figures in Table 148 indicate.

TABLE 148.—*World production of pig iron, including ferro-alloys, in metric tons.**

	1944	1946
United States	57,059,457†	42,023,299
United Kingdom	6,844,621	7,885,564
France	1,126,903	3,502,000
Germany	13,370,000	2,322,000
Belgium	718,490	2,170,790
Canada	1,836,088	1,379,597
Luxembourg	1,348,096	1,364,400
India	1,453,713	1,347,000
World	103,000,000	80,000,000

In 1947, the pig iron production in the United States was 54,534,995 metric tons; in 1948, about 1 million tons more.

* "Minerals Yearbook.
† Peak figure. The peak for world production was 111,500,000 metric tons in 1942.

The process in brief consists of heating an iron ore, an oxide, with coke in an upright furnace having continuous operation; hot air under pressure is pumped into the furnace at the base, and by causing the coke to burn, produces a high temperature. The iron oxide is reduced to the metal which collects at the lowest spot, and is tapped off at intervals; the hot fluid iron unavoidably dissolves some carbon (3 per cent). The solids added at the top are iron ore, coke, and limestone; the latter binds much of the silica present as impurity in the ore, and forms with it and other substances the slag, which flows to the bottom of the furnace. The liquid slag is lighter than the liquid iron and floats on it; it is tapped at frequent intervals through a special tap hole, further up than the iron tap hole. Almost without exception, a mixture of several kinds of ores is preferred to a single one.

The oxide richest in iron is magnetite (Fe_3O_4) with 72.5 per cent; it is found very pure in Sweden and in a few places along Lake Superior.[1] The next oxide (Fe_2O_3), hematite, nearly as rich in iron (70 per cent when absolutely pure), is the most important. It is the ore which made the Mesabi range famous. 88 per cent of the 1946 production was hematite; 7.3 per cent was magnetite (U. S.). The production of crude iron ore by regions follows:

[1] Magnetite deposits occur also in New York, Pennsylvania, New Jersey, New Mexico.

TABLE 149.—*Production of iron ore in the United States, by region, and by method of mining (crude ore, in gross tons).**

	1943	1946
Lake Superior	95,586,789	67,014,550
Southeastern	14,051,854	9,278,832
Northeastern	7,018,617	5,136,313
Western	3,017,720	2,764,786
Total	119,674,980	84,194,481
Open-pit mining	86,849,778	63,859,082
Underground	32,825,202	20,335,399
Average value at the mine	$2.70	$3.07

The production in 1946 came from 191 mines; of the total ore, 68 per cent came from Minnesota, 10.3 per cent from Michigan, 9.4 per cent from Alabama, and 5.11 per cent from New York and Pennsylvania, mainly the former.

* Minerals Yearbook.

An extensive deposit of hematite generally containing some phosphorus stretches from New York State to Alabama, and is mined in several of the states it traverses.

Much concern has been expressed over the prospect of the exhaustion of our domestic iron ore deposits, especially in the Lake Superior region. The withdrawal of ore during the war years was serious; for example, in 1942 141,710,416 short tons of domestic iron ore were produced (of which 49,936,513 tons were sent to beneficiating plants). The estimated reserves in Minnesota and Michigan together are placed at 1,015,438,281 gross tons, which would constitute a 12 to 15 years' supply. Fitting in with the concern over depletion is the relative amount of ore being beneficiated; in 1925-29, the percentage of beneficiated ore in the total shipping ore was 13; by 1945, it had risen to 22.4.

There are two ways to prepare for a shortage; one is to import ore, the other to use lower-grade ores. A possible source of imports is the Ungava deposit of high-grade ore discovered near Burnt Creek, on the border of Quebec Province and Labrador, about 650 miles north of Quebec, and about 360 miles north of Seven Islands, the nearest port on the Gulf of St. Lawrence. At present, the site is accessible by air only. Another potential source is a deposit north of the Amazon in Brazil. Such newer supplies would supplement the present well established imports from Canada, South Africa and Europe. Imports from Cuba, temporarily discontinued, are coming in again. A new development in Venezuela will furnish a sizable tonnage of ore each year.

Taconite is a lower-grade ore (20 per cent iron and higher) of which billions of tons are available in the Mesabi range, Vermilion and others near by. Taconite is a hard rock, in which it is difficult to drill blast holes. This difficulty has been removed by the advent of fusion-piercing, in which a hole is burned in the rock by means of a rotating multiple-port blowpipe; the drillings are blown out by steam produced by the flame on a stream of water introduced behind the torch. All of the taconite will have to be beneficiated, at a cost estimated to be $2 a ton.[2]

In the course of beneficiation, the valuable portion of the ore is concen-

[2] The first pig iron from taconite in Minnesota was reported on May 30, 1948.

trated, and the gangue (waste material) is discarded; hence a shrinkage in weight takes place. Roughly about 2 tons of crude ore furnish one ton of concentrate.

The average analyses of total tonnage of all grades of iron ore from all ranges in the Lake Superior district for 1946 was as follows: Fe, 51.32 per cent; P, 0.087 per cent; SiO_2, 8.83 per cent; Mn, 0.74 per cent. The iron content is reasonably good. In 1941, for comparison, the ore contained 52.43 per cent Fe. The price of 51.5 per cent Fe ore was $6.20 in May, 1948, representing a sharp rise over 1946.

Only ores which are low in phosphorus can be used in the acid Bessemer or acid open hearth, as shown in Table 150. A second impurity of commanding interest is manganese, which must not be too high; it is kept within limits by proper mixing of different ores.

TABLE 150.—*Iron ore analyses on the natural ore.**

	Mesabi range Bessemer grade	Mesabi range Non-Bessemer grade	Cuyuna range Manganiferous
Iron, Fe	52.10%	54.99%	42.60%
Phosphorus, P	.035	.071	.190
Silica, SiO_2	11.00	4.15	11.80
Manganese, Mn	.40	.44	3.40
Alumina, Al_2O_3	.65	1.27	1.80
Lime, CaO	.15	.14	.44
Magnesia, MgO	.14	.11	.18
Sulfur, S	.016	.016	.011
Loss on ignition	5.20	4.14	6.14
Moisture	8.23	10.77	11.64
Name of ore	Bassano	Beaver	Alstead

* From "Analyses, iron ores, 1949," The M. A. Hanna Co., Cleveland, O.

In addition to beneficiation, certain ores without or with prior beneficiation are sintered in order to change a fine ore into granules or agglomerates large enough to resist the blast in the furnace.

As an example of American mining and shipping practice, the operations at the Fayal mine in northern Minnesota, about 60 miles from the lake shore (Two Harbors), and part of the Mesabi range deposit, will be briefly described.

The Fayal mine is an open pit mine; the removal of about 20 feet of overburden discloses a vast body of red ore, most of it soft enough to work with a steam shovel. Various levels are worked, as the quality differs slightly; movable railroad tracks are laid on inclines. The empty ore cars are pulled to the desired spot, where a steam shovel (or several) awaits them; the cars are loaded in a short time, without hand labor. A powerful locomotive pulls the cars up the incline and starts toward the lake port, Two Harbors. The train passes at a slow rate over scales, and the weight is read and recorded as the train moves. By the time it reaches Two Harbors, the chemical analysis of the loaded ore is finished and its exact grade determined; this permits a train dispatcher to send the cars to certain pockets in a certain dock, there to be dumped with similar ore. The cars are dumped by pulling the level which opens the bottom. The ore boats are loaded in a simple but rapid way. The ore pockets in the docks are elevated,

so that by lowering a chute and drawing a gate, the ore is served to the boat by gravity. On approaching, the lake boat whistles its requirements as to quality; a siren at the end of the central dock screeches back signals which tell the boat at which dock, and in front of which pockets in the dock, it should anchor. The boat pulls in with its hatches open, and while still being anchored, the chutes are lowered and the ore rumbles into the boat. In thirty-nine minutes it can be on its way out with a load of 11,000 long tons.

In the order of tonnage of pig iron produced, the producing states are as follows: Pennsylvania, Ohio, Indiana, Illinois, Alabama, New York, West Virginia (1946). It will be noted that the centers of production are those which have coal and coke, rather than ore, or together with ore; it is a general rule that "ore follows the fuel." The primary production district since coke displaced charcoal and anthracite is Pittsburgh, where Connellsville beehive coke was available. The Minnesota ore was transferred to railroad cars at near-by lake ports for the short haul to the Pittsburgh and Youngstown districts. This is still done, but more and more plants have been located at the lake ports, so that the ore boat might unload directly in the yard of the blast furnace plant (Buffalo, Cleveland, Detroit, Gary, Chicago). It is to the interest of these Lake plants that abundant ore be obtainable from mines along Lake Superior or Michigan, or otherwise favorably situated.

In Alabama (at Birmingham and other places) the ore and the coal are both found in the district, and in addition the ore contains enough limestone to be self-fluxing. Alabama ore, however, is lower in iron content than the best Lake Superior ore (35 per cent against 52 per cent). An agency which is at work decentralizing the pig iron industry is the by-product coke oven primarily set up to provide municipalities with gas; it generally has surplus coke suitable for the blast furnace. Along the Atlantic seaboard (Baltimore, Philadelphia) ore from Cuba, even from Sweden, Elba, Spain, and Chile, may be imported at reasonable cost, and with the aid of by-product coke, made into pig iron.[3]

In England, very pure ores free from phosphorus are mined; with the rich coal resources of Great Britain, the iron industry has long flourished. France has in the Lorraine deposits a large tonnage of low-grade (30 per cent Fe) ore which contains phosphorus, but also calcium carbonate, so that by skillful working a phosphorus-containing pig iron suitable for the basic Bessemer process for steel, can be made. The deposit is 30 miles long and 12 miles wide, and in its eastern part is mined at the surface. The greater part of the pig iron and steel production of France and Germany comes from this Lorraine ore.[4] In Sweden, very pure iron is made with charcoal, from native ores; this pure product is still the basis of the cutlery manufacture of

[3] Bethlehem, Pa., is not too far from seaboard to use foreign ores mixed with western Pennsylvania ores.

[4] A portion of the deposit lay in the part of Lorraine held by the German empire during 1871 to 1918; its importance was unknown in 1871, for it was only after the English improvement of the Bessemer process, the Thomas-Gilchrist basic lining, that the Lorraine ore could be made into good steel; the effect is plain from the German production figures for steel: 1880, one-half million tons; 1913, 18 million tons. The following figures will indicate the quality of the ore for the Lorraine district, more particularly for the Landres basin, one of the 4 main divisions: Fe 40%, CaO 10%, SiO_2 6%, Al_2O_3 7%, P 0.65%.

Sheffield. In southern Russia, iron is produced in considerable quantities.[5] China has rich ore deposits, while her coal resources are second only to those of the United States.

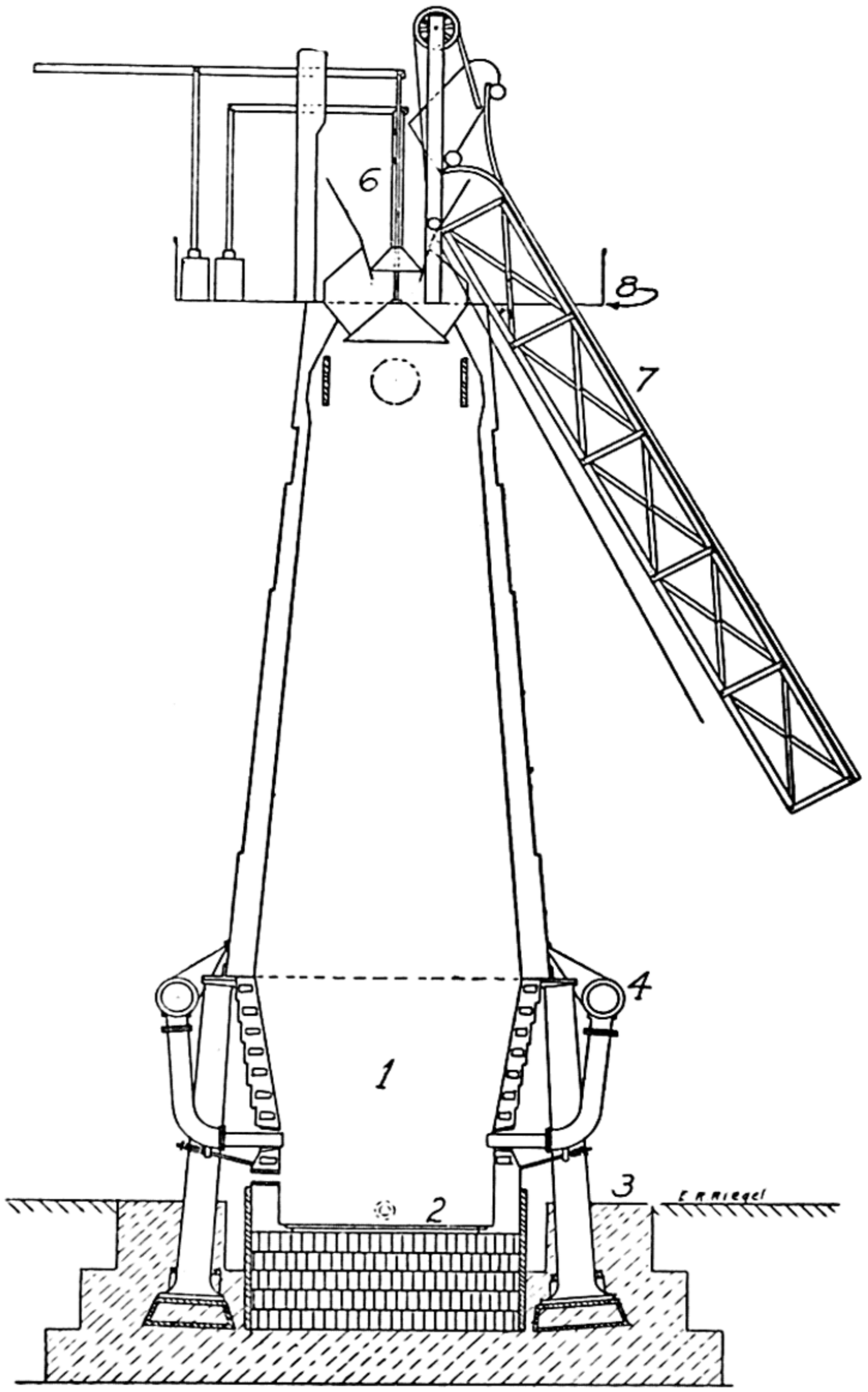


FIGURE 333.—The blast furnace for iron, showing the furnace proper, with 1, the bosh; 2, the hearth; 3, the foundation; 4, the bustle pipe and tuyeres; 6, the double bell for introducing the charge; 7, the skip hoist; 8, platform at top of furnace. The dotted circle under the bell is the outlet for the gases. The distance from 8 to the hearth line at 2 is 92 feet.

THE BLAST FURNACE

The complete blast furnace plant consists of the furnace proper, four stoves, a dust collector, a blowing engine, means of bringing the solids to be charged to the skip hoist, and auxiliary apparatus.

The blast furnace proper consists of a steel shell circular in cross-section,

[5] 150 miles northeast of Odessa west of the Dnieper, in western Ukraine, lies the Krivoy Rog district, which came into the news in August, 1941, when the Germans claimed its capture. It was said at that time that 61 per cent of the Soviet Union's iron ore output came from this district. In 1938, the production had been 16 million tons of ore.

lined with hard fire-brick; the shell stands upright; the upper two-thirds or so flare out downward, while the lower third flares in. The purpose of the upper flare is to permit the charge to slide down readily and fill any holes which might develop; with straight sides, it often happened

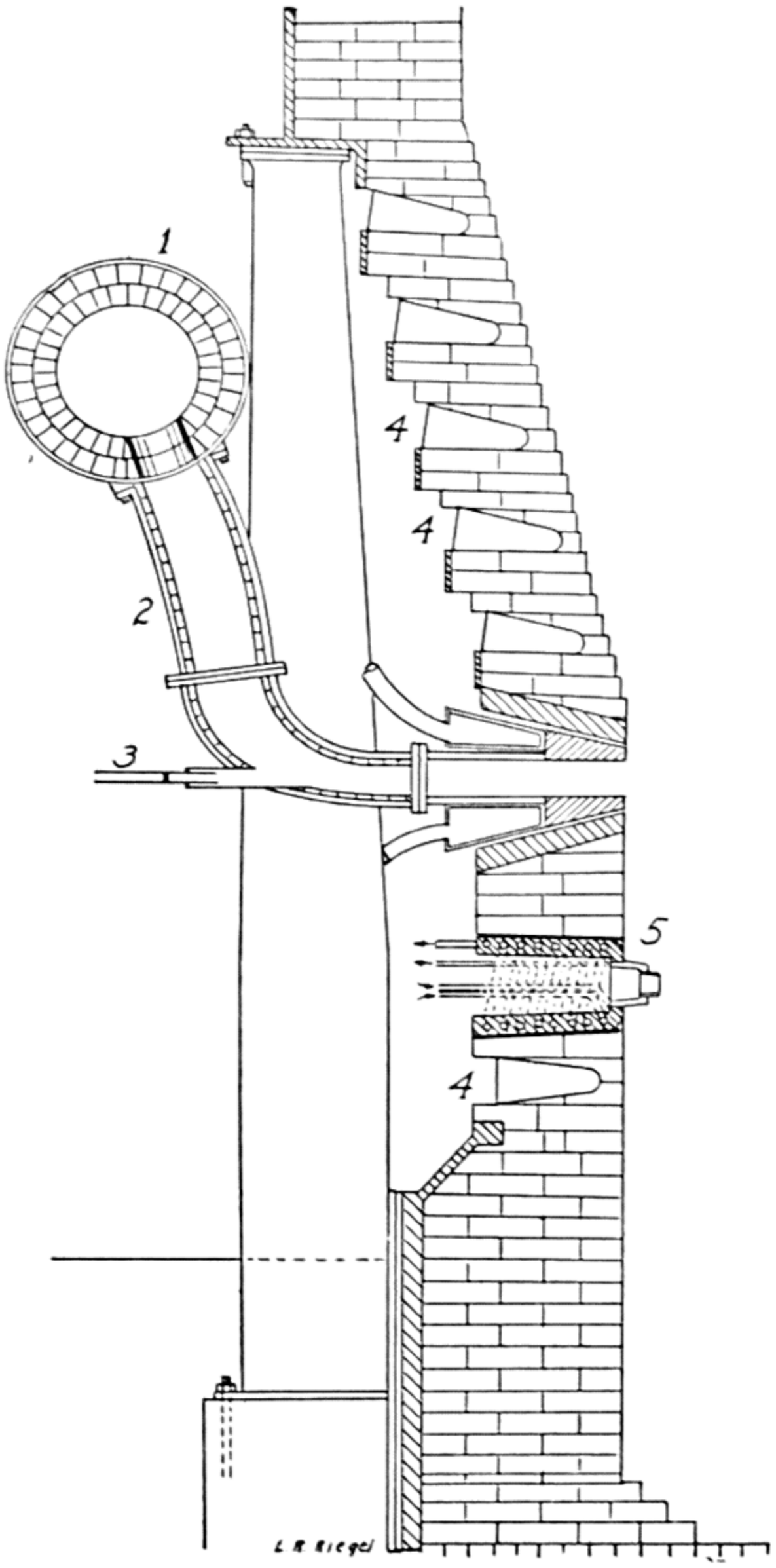


FIGURE 334.—Section of the bosh wall in the blast furnace for iron, with 1, bustle pipe; 2, tuyere; 3, sight hole; 4, water-cooled metal boxes; 5, slag hole with water-cooled metal lining.

that large cavities formed, so that after a while a sudden descent (a slip) took place, which at times proved disastrous. The lower flare in the opposite sense is required by the removal of the coke by combustion, and the running down of the melted iron, causing a great contraction. The bottom of the furnace is the hearth, where the liquid iron, overlaid by the liquid slag, collects. The charge in the furnace is called the "burden,"

and is introduced at the top through a vestibule-like arrangement which prevents the escape of gases; the materials fall first onto an upper bell, which is depressed in order to allow the materials to drop into the intermediate chamber whose floor is formed by a second bell. When the second bell is depressed, the charge enters the furnace; at such times, the upper bell is shut tight. This bell is also rotated, so that the charge is placed evenly over the surface of the furnace content. The liquid iron and the liquid slag are removed periodically by tapping. Tne slag hole is formed by a water-cooled metal piece, situated above the iron hole; the taphole for iron is in brickwork. At the end of the tapping, the iron hole is closed by a plug of clay, applied by the "mud gun," with a fast-moving piston which forces the clay into the hole. The slag hole is easily closed by an iron plug on a long rod.

The air blast for the combustion of the coke enters through the bustle pipe, a steel pipe 3 feet in diameter lined with fire-bricks, because the air is applied very hot (between 1600 and 1000° F.). The blast passes from the bustle pipe to the furnace through the tuyeres, which are partly lined and partly water-cooled. Each tuyere has a sight hole and may be cleared by a rod if anything blocks it from the inside.

The hottest part of the furnace is the bosh (see illustrations) where the tuyeres deliver the blast, and intense combustion of the preheated coke takes place.

The weight of the upper part of the furnace is carried by a number of columns (12 to 18) resting on an elaborate foundation on which the bosh also rests.

The furnace shown in Figure 333 is 92 feet high and 23 feet in diameter at the widest part. In Figure 334, a closer view of the bustle pipe, tuyeres, slag hole, and bosh wall is given; it will be noted that the bosh wall carries metal boxes which are water-cooled, thus lowering the temperature of the brickwork and rendering it more lasting.

The Materials Supplied to the Furnace. Let us consider a blast furnace which produces 1150 tons of pig iron per day. Such a furnace would be a large one, but not the largest. The solid materials fed in per day are as follows: coke 850 tons, limestone 400 tons, ore 2000 tons, divided into 112 charges per day. There are besides occasional additions, such as: every second charge, open-hearth slag, 6000 pounds; every third charge, 5000 pounds of borings; every fifth charge, 1000 pounds of ore containing 5 per cent manganese; and every fifth charge also 1000 pounds of siliceous ore.

The average consumption of ore per ton of pig iron made in the United States in 1945 was 1.870 tons.

The hot blast which enters the furnace is equivalent to 4040 tons during the day; the rate is 80,000 cubic feet per minute. The pressure is 18 pounds. The air is forced into one stove where its temperature is raised at first to 1400° F., then to 1200° F., finally to 1000° F. as the stove gradually cools. After an hour, the air is turned into another stove which in the meantime has been brought to its highest temperature. Four-fifths of the weight of the blast nitrogen takes no part in the reaction. It will be noted that the air fed to furnace exceeds the solids in weight.

The stoves are tall steel chambers, lined, and filled with a checkerwork of firebricks, in which blast furnace gas is burned with cold air for 3 hours; the bricks gain in heat. Each stove receives heat for 3 hours, and gives up heat over a 1-hour period. If No. 1 is heating the blast, No. 2 is receiving its third hour's heating, No. 3 its second, No. 4 its first. The stoves are of various constructions, but all have an internal downcome; the waste gases may travel through the downcome leading to a chimney, or may leave by a stack surmounting the stove.

The Reactions in the Furnace. The main reaction in the blast furnace is the reduction of iron oxide to the metal. Coke burns in the hot blast as the latter is led in by the tuyeres, forming carbon dioxide, and the latter is reduced almost at once by the hot carbon adjacent to carbon monoxide. The flames at the mouths of the tuyeres extend over a comparatively limited zone. The carbon monoxide rises and much of it, about a third, functions as the reducing agent:

$$Fe_2O_3 + 3CO \rightarrow 3CO_2 + Fe_2$$

The balance passes to the top of the furnace and passes out in the blast furnace gas, to which it imparts most of its calorific value, unchanged. The simple reaction is an overall result, and a summary of numerous others.[6] It is very likely that free iron in the spongy form is first formed and melts only later when it passes through the lower part of the bosh; and it is also held that the first reduction is to a lower oxide, which is then later reduced to the metallic iron. The liquid iron contains carbon to the saturation point, in solution, and some in combination.

The limestone loses carbon dioxide, and the lime formed reacts with part of the silica to form calcium silicate:

$$CaO + SiO_2 \rightarrow CaSiO_3.$$

No appreciable amount of iron silicate forms because the lime displaces the iron, thus preventing a loss of metallic product.

The phosphate is present as calcium phosphate, and in presence of silica, the free phosphorus is liberated and dissolved by the iron:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + 4P + 10CO.$$

Silicon is formed from such silica as may reach the hottest region where the combined action of iron and carbon reduce it to the free elements:

$$SiO_2 + 2C + (Fe) \rightarrow Si + 2CO + (Fe).$$

Manganese is reduced by carbon at the high temperature of the bosh. Both silicon and manganese are dissolved by the iron. Sulfur, partly if not all from the coke, forms ferrous sulfide which is so heavy that it mixes with the iron layer, and not with the lighter slag layer.

The maximum temperature in the furnace, at the tuyere line in the lowest portion of the bosh, is generally held to be 2800 to not quite 3000°

[6] "Blast Furnace Practice," by Ralph H. Sweetser, p. 159, New York, McGraw-Hill Book Company, 1938.

F. (1538 to not quite 1649° C.). It then gradually decreases as the gases rise in the shaft of the furnace, until at the top the gas leaving the furnace has a temperature of 400° F. (204° C.). Most of the sensible heat in the gas is transferred to the cold charge, so that the blast furnace is well named when it is called a heat interchanger; with the blast furnace gas in mind, it might be said also that it is a large-scale gas producer.

Tapping the Furnace. The furnace is tapped for iron five times a day, for example. The iron hole is broken free of the dried clay, and the molten iron flows out along a gutter lined with firebrick; it passes a small roughly made bridge with retaining box; under the bridge the clear iron flows on; over the bridge any slag which was entangled in the metal flows off through a sidewise gutter. The clear metal reaches brick-lined steel ladles capable of holding 70 or 100 tons of metal. Near the end of the tap, the blast is shut off, and when the flow of metal becomes lazy, the clay plug is rammed into the hole. Operation is then resumed.

The slag is tapped every two hours, through its own hole, situated a quarter of a circle away from the iron hole, as well as farther up. The slag is run through a gutter in the floor to a large container on a flat car and pulled to the dump heap, or to a near-by cement plant where it is granulated by cold water and used as one of the raw materials for making a portland cement; there are still other uses for the slag.

The products of the blast furnace thus are pig iron, slag, and blast furnace gas.

The composition of ordinary pig iron lies within the following limits:

Carbon	3 to 4%
Manganese	0.25 to 2½%
Sulfur	less than 0.065%
Silicon	0.5 to 3%
Phosphorus	0.04 to 2%
Iron	balance, about 92%

There are other "metals" made to suit the orders and purposes.

The Pig Casting Machine. The ladle is carried by the crane to the casting machine and there tilted forward so that the metal is delivered to a box with two side outlets. The box divides the metal into two streams, which feed the buckets of the two endless chain conveyors. A spray of water is played on the slowly traveling buckets, which congeals the iron sufficiently so that at the turn they drop off, still red, as cakes and slide into a waiting car, where they cool to blackness with the aid of more water. Each pig weighs 110 pounds and is 22 inches long, 7 inches broad at the base, and 4 inches thick.

In many blast-furnace plants, there is no need of casting the metal into pigs, for it is to be used at once for steel making in the open hearth, or in the Bessemer converter. For such purposes the iron is never taken directly from the blast furnace to the steel furnace or converter, but it is delivered first to a very large ladle capable of holding several taps; this large receiver is called the mixer. It offers the great advantage of furnish-

ing a very uniform metal, avoiding single taps with just enough irregularity of composition to prevent the metal from giving the usual results. In some installations, the mixer is more elaborate still and the opportunity is taken to burn off some of the sulfur by playing a stream of burning gas over the surface.

The Blast Furnace Gas. The gas which passes out at the top of the furnace has been cooled considerably by the cold portion of the burden, which gains the heat which the gas loses. The gas is cold enough to be passed through a steel flue to a steel dust-catcher, and from there to a gas washer, a box through which a fine spray of water descends, while the gas ascends. The cleaned gas is made to work in several ways: to raise steam for the driving of the blowing engines, as internal gas fuel for the gas engines driving the air compressor, if such are used, and to heat the stoves so that by means of the latter the incoming blast may be heated. The gas is not rich in combustibles, but it contains enough to furnish the heat required for the purposes stated above; usually there is surplus gas, which in some cases is piped to households of employees. The heat value of the gas[7] is due to its carbon monoxide content:

	Per cent
Hydrogen, H_2	1.0
Nitrogen, N_2	59.6
Carbon monoxide, CO	26.0
Carbon dioxide, CO_2	13.4
B.t.u. of the blast-furnace gas	87

Pig iron prices are different for the six varieties cited; in 1946, Bessemer pig was $28.18 a net ton, while the basic pig, produced in the largest quantities (34,131,539 tons) was $24.25. The average price for all grades[8] was $24.49. Since then, the price has risen sharply; the figure for Number 2 foundry, Philadelphia, in 1947, was around $36.50, in 1948, around $51.50, and this was still the price in February 1949. One cause for the rise is the higher price for coal, and hence for coke (which see).

By operating the blast furnace under a pressure of 10 lbs./sq. in. above the usual pressure, which is essentially atmospheric, the production of iron per furnace per day is increased substantially, while the consumption of coke per ton of pig is decreased by 250 pounds. The reactions are accelerated, but the temperature in the furnace is not raised.[9]

Plans to enrich the blast served the furnace by means of oxygen (tonnage oxygen) have been advanced; one advantage would be the increased production per unit space of furnace. It remains to be established how high an increase in temperature will take place, and how it can be allowed to develop without damaging the furnace.

The making of iron castings is described in Chapter 45.

[7] Other types of commercial combustible gases will be found in Chapter 15. Other analyses of blast-furnace gas will be found in *Chem. Met. Eng.*, 10, 713 (1912).

[8] For grades of pig iron, see "Standard grades of pig iron," in "Steel Products Manual," Section 1, American Iron and Steel Institute, June 1, 1941, New York 1, N. Y.

[9] Scientific American, May 1948, p. 54.

Sponge Iron [10]

Sponge iron is made by reducing finely divided iron ore to the metallic form without melting the ore or the product. A soft iron results which contains whatever impurities were present in the ore. By using Swedish ore, and some of the New York State ores, a pure sponge iron can be produced. During the war, it was hoped that sponge iron might supplement steel scrap, which was short, but the enterprise was only partly successful. In one installation sponsored by the Government, the ore was reduced by hydrogen and water gas in a continuously operated, alloy-steel shaft furnace. There is at least one furnace in operation in which natural gas is the reducing agent. It would seem, however, that sponge iron will not be an important material in the iron and steel industry.

Wrought Iron

The earliest form of iron, obtained from the oxide ore by heating it with charcoal to the softening point, and then laboriously worked over ("puddled") at the heating place by handtools, with the metal never free from slag, lost its importance with the installation of the processes which produce liquid steel and liquid cast iron. Nevertheless, wrought iron is still being made, mainly because it has high corrosion resistance. Hand puddling was succeeded by mechanical puddling, itself supplemented by fagoting; the most modern and striking method, with rapid and high output, is the Aston [11] process, also known as the Byers process.

Wrought iron is defined as a ferrous material, aggregated from a solidifying mass of pasty particles of highly refined metallic iron with which, without subsequent fusion, is incorporated a minutely and uniformly distributed quantity of slag. It is the presence of the slag which gives it its fibrous structure.

In the Aston process, the pig iron is melted in cupolas and blown in Bessemer converters according to the usual practice for steel (see next chapter). The blown metal is tapped into a ladle, then poured into molten slag contained in the processing ladle. The slag is held at a temperature several hundred degrees lower than the freezing point of the refined metal; the latter is continuously and rapidly solidified. Such rapid solidification causes the dissolved gases to burst out with sufficient force to shatter the metal into small fragments which settle to the bottom of the ladle, where they weld together, aided by slag particles, into a sponge. At once the excess slag is poured off, and the sponge ball (6000 to 8000 lbs.) dumped at the rate of one every five minutes on a platform of a 900-ton press, where it is squeezed into blooms ready for rolling.[12]

[10] "Production of sponge iron," R. I. 4305, E. P. Barrett and C. E. Wood, Bureau of Mines. "Experience to date on iron production by methods other than coke blast furnace; direct reduction," Earle C. Smith, Reports of Amer. Iron and Steel Institute, May 26, 1948, New York Meeting. See also article in *Min. Metallurgy*, Sept. 2, 1942, p. 467, by Clyde Williams.

[11] The patents granted to James Aston, on the manufacture of wrought iron, are: U. S. Patents 1,255,499; 1,413,513; 1,820,177; 1,890,637; 1,987,598; assigned to the A. M. Byers Company, Pittsburgh, Pa.

[12] *See* chapter on "Wrought iron," by A. W. F. Green, "Metals Handbook," 1936, Cleveland, O., pp. 337-343.

Wrought iron has low carbon and low manganese content. For example, Byers No. 1 contains C 0.08 per cent, Mn 0.015 per cent, Si 0.158 per cent, P 0.062 per cent, S 0.010 per cent, slag by weight 1.20 per cent.

The production of wrought iron pipe and tubing, the most important outlet, is in the neighborhood of 50,000 tons a year. The corresponding articles made of steel total about one million ton a year. Plates, sheets, bars and other products are also made of wrought iron to a limited extent.

Other Patents

U. S. Patent 2,057,919, influencing the chemical and physical properties of blast furnace slags; 1,984,793, production of pig iron and Portland cement in a blast furnace; 1,941,983, reducing iron ore; 1,964,402, same topic; 1,963,269, desulfurizing and purifying iron; 1,837,696, electro-thermic reduction of iron ores: Ore, carbon, and flux are introduced into a horizontal hollow graphite electrode; the charge is pushed gradually down the passage, gaining in heat, until the hottest zone at the mouth of the electrode is reached, where reduction takes place. The melted iron (cast iron composition) collects in a fore-chamber, which is tapped at intervals.

Problems

1. In the present chapter, is there an example of the countercurrent principle worth mentioning?

2. Let the ore charged in the specific example for the blast furnace given in the text, contain 50 per cent Fe, and assume that the dust loss is nil, also that there is no other loss; compute the weight of iron which will be obtained, assuming the pig to be 92 per cent Fe.

3. Set up figures to show how many tons of the several materials are required to make one ton of pig iron, from information given in the text.

Reading References

"The blast furnace and the manufacture of pig iron," Robert Forsythe, David Williams Co., New York, 1922.

"Index to iron and steel patents," V. Everett Kinsey and Thomas E. Hopkins, American Compilation Co., Pittsburgh, Pa., 1931.

"Principles of the metallurgy of ferrous metals," Leon Cammen, American Society Mechanical Engineers, New York, 1928.

"Slag viscosity tables for blast-furnace work," Bur. Mines, Tech. Paper 187, 1918.

"The basis for desulfurization of pig iron and steel," P. Bardenheuer and W. Geller, *Kaiser Wilhelm Inst. Eisenforchung*, Düsseldorf, 16, 77-91 (1934).

"The iron furnace," T. L. Joseph, *U. S. Bur. Mines I. C.* 6779 (May, 1934). See also *R. I.* 3229, and *R. I.* 3240.

"Blast furnace practice," Ralph H. Sweetser, New York, McGraw-Hill Book Co., 1938.

"The making, shaping and treating of steel," J. M. Camp and C. B. Francis, 5th edition, Pittsburgh, Pa., Carnegie-Illinois Steel Corporation, 1940. *Pig iron*, p. 223-297.

The production of steel in 1940, for the United States, was 67 million short tons. In 1942, it is expected that the production will not be far from the rated capacity, 91.1 million tons per year. The making of steel on this huge scale is an industry only about 72 years old; it dates from the invention in 1855 by Henry Bessemer, an Englishman, of a new method of purifying pig iron, the usefulness of which was extended (1878) by Thomas and Gilchrist, also Englishmen. The process of Bessemer was discovered independently by William Kelly, of Kentucky, in 1847. The other main process for steel is due to William Siemens, an Englishman, and to E. and P. Martin of France (1865). Several of the important improvements of a later date are due to Americans.*

Chapter 48

Steel

Steel is a purer iron than cast iron; the undesirable impurities of the latter, silicon, phosphorus, sulfur, and manganese, are either removed or reduced to a very low amount except on special orders; carbon, which is 2.5 to 4 per cent in cast iron, is reduced to 0.2 per cent for a very soft steel, 0.55 for rail steel, and perhaps 1 per cent for extra-hard steel, in all cases distinctly lower than in cast iron. It will be noted that the amount of carbon in the steel, varying between the comparatively narrow limits of 0.20 to 1 per cent, regulates the hardness of the steel. The manufacture of steel is then essentially a purification of pig iron, by slagging the phosphorus, silicon, and manganese, and removing the excess carbon by oxidation; the raw material is not pig iron alone, but to a large extent steel scrap of all kinds. The proportions of pig iron and scrap are not fixed but depend upon market conditions. The removal of the impurities effects a profound change in the properties of the material; the brittle, comparatively weak cast-iron, which cannot be rolled, is transformed into the strong, tough steel, which may be rolled and forged while at red heat. The melting point rises. Table 151 shows the difference in some of the properties.

Steel has the further advantage of acquiring a "temper," varied according to the details of treatment, by heating and quenching; heating and slow cooling removes the temper.

The steel produced on a large scale has become a structural material of first importance, replacing stones and bricks, and making possible the building of bridges which otherwise would not exist. The American skyscraper would have been impossible without steel. The extension of railways is due also to the large-scale production of steel, not only for the rails, but also for the locomotives. Stationary high-pressure boilers, steam

* U. S. Patents to William Kelly, 16,444 (1857), combination of the hearth of a blast furnace with auxiliary tuyeres bringing a blast of air; 17,628, blowing blast of air, hot or cold, through a mass of liquid iron, the oxygen combining with the carbon, causing a greatly increased heat and boiling commotion in the fluid mass and decarbonizing and refining the iron; 18,910, claim 1, conducting a blast down through the liquid iron to near the bottom of the hearth; claim 2, refining and decarbonizing simultaneously in the hearth of a blast furnace and in an adjoining chamber having communication therewith.

TABLE 151.—*Properties of iron and steel.*

	Specific Gravity	Tensile Strength Pounds per sq. inch	Melting Point ° F.	Melting Point ° C.	Carbon Content *Per Cent*	May Be Rolled
Pig iron (gray)	7.3	15,000	2000	1093	2.50–4.00	No
Medium steel	7.8	65,000	2500	1371	0.15–0.30	Yes
Rail steel	7.8	110,000	2500	1371	0.55	Yes

engines and turbines, machines of all kinds depend upon the production of steel. The two processes by which such steel is produced are the Bessemer converter process and the open hearth process; the two produce essentially the same kind of steel.

There are in addition a large number of special steels, with properties suiting specific purposes, many of them of great importance, although the tonnage used may be small. Examples are: self-hardening tool-steel, nickel steel for armor-plating, chrome steel for navy guns; these will be described briefly further on, and also the process of combining a hard surface with a tough, strong interior, by case-hardening.

OPEN HEARTH PROCESS

The open hearth process was introduced some 10 years after the Bessemer converter. The charge is placed on the hearth of a large brick furnace heated by gas or oil fire, and the heating continued, with occasional

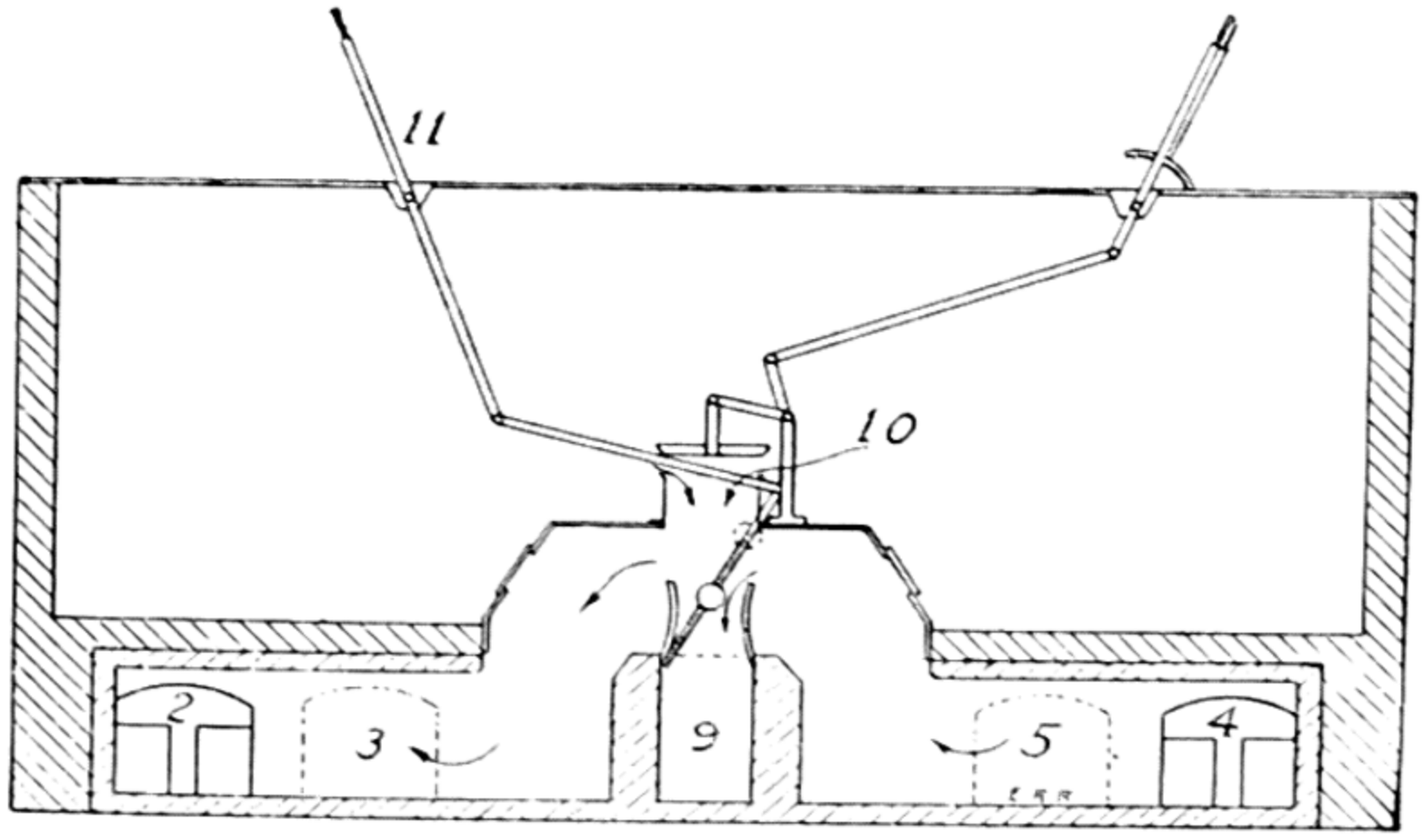


FIGURE 335.—Air reversing mechanism; 10, entering cold air; 3, regenerator for preheating the air; 5, fire gases leaving the second regenerator for air, and passing to the stack at 9; the butterfly valve is reversed at 11. A valve for controlling the amount of air is also provided.

additions of fluxing materials, until the carbon is sufficiently low; the product is tapped at intervals.

As example of open hearth furnace practice, a specific furnace with a hearth 19 feet broad by 34 feet in length, with a capacity of 100 tons every 11 hours, will be described. The hearth is on a level with a working floor sufficiently elevated so that on tapping, the metal may be run into a

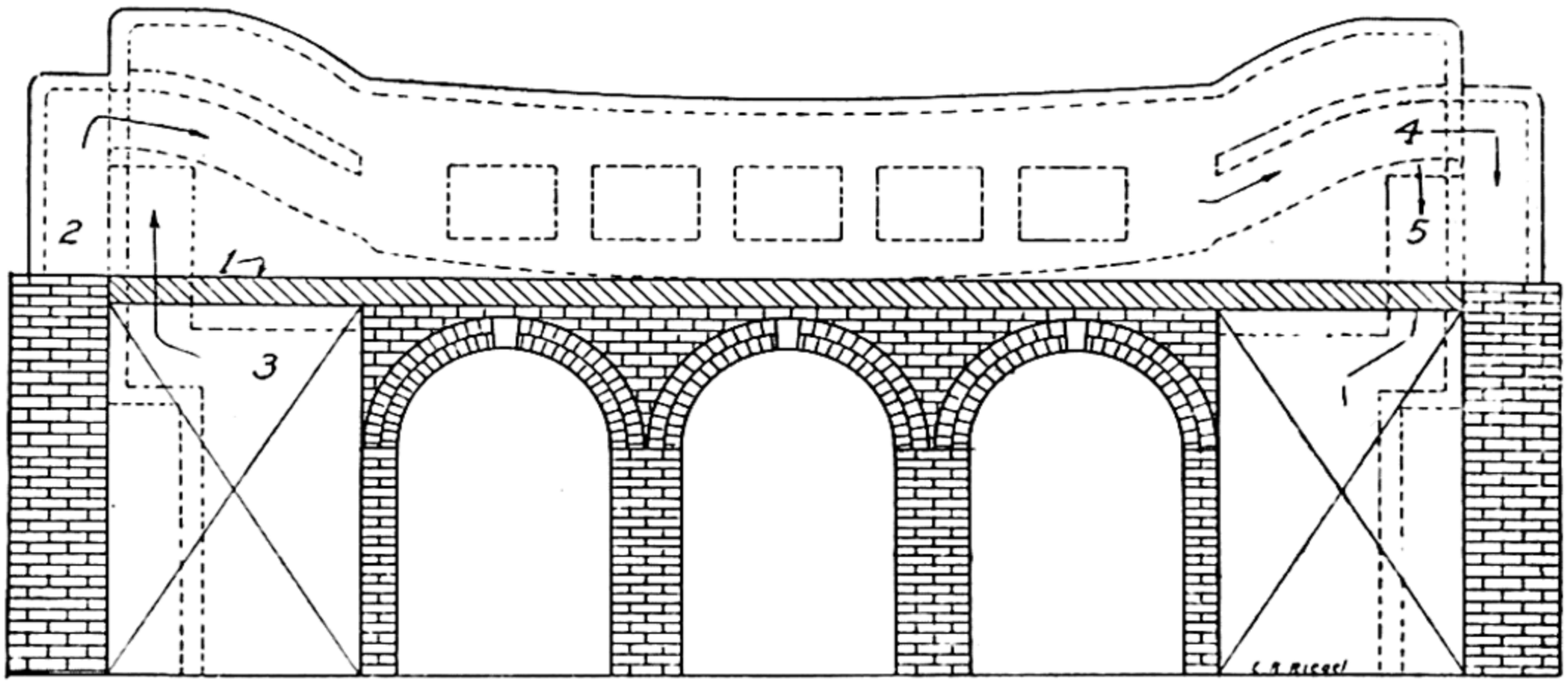


FIGURE 336.—Front view (elevation) of the open hearth furnace for steel. 1, working floor; 2, entering hot producer gas; 3, entering hot air blast; 4, fire gases passing to regenerator for gas, and 5, for air. The same numbers for blast and air are used in the several sketches.

receiver, the ladle, standing on the ground floor; this provides at the same time space under the furnace for the brickwork of the regenerators. The fuel is producer gas,[1] preheated in a regenerator; the air is also preheated. Air and gas enter by separate ducts at the left of the furnace, mix, and sweep while burning over the hearth, and pass out at the right, reaching two regenerators which they heat, before escaping to the stack. There are in all 4 re-

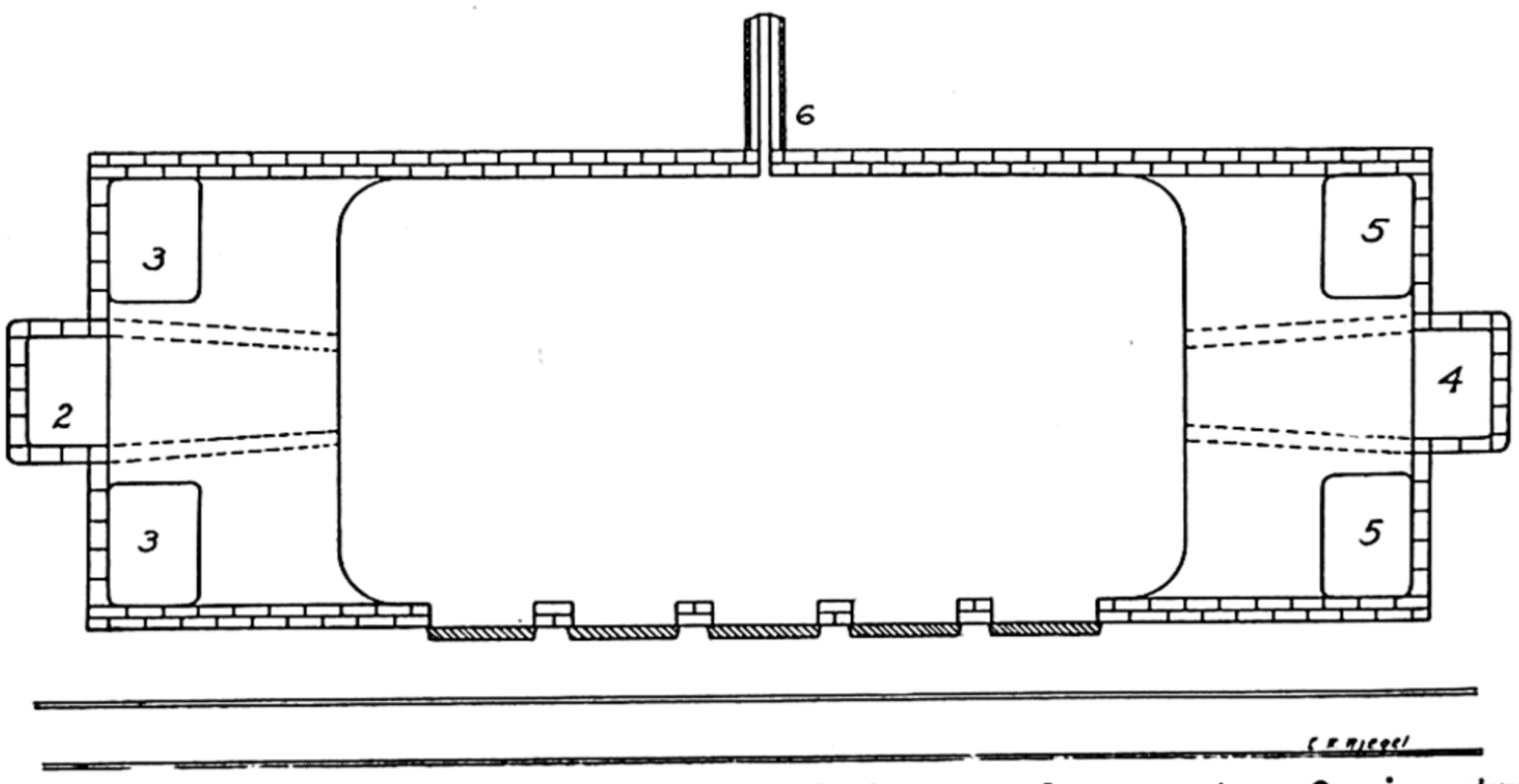


FIGURE 337.—Floor plan of the open hearth furnace; 2, gas entry; 3, air entry; 4, fire gases to gas generator; 5, fire gases passage to air regenerator; 6, tapping trough, at the rear of the furnace.

generators to each furnace; the direction of the gas and air is reversed every 15 minutes, by hand operation of levers which control the compressed-air mechanism which swings the valves. A scheme for the reversal of the air is shown in Figure 335, a second similar arrangement reverses the gas flow.

[1] Chapter 15.

Several views of the furnace (Figures 336-338) will add to the description. The roof of the furnace is rather high (8 feet) in order to give room for the charging pans. The doors are water-cooled steel doors, operated by compressed-air mechanism with distant control.

The furnace has 5 working doors which face the working platform; all the work is done on this side except the tapping, which is done at the rear (*compare* Figure 338). The furnace floor is built of clay bricks, covered with magnesite bricks,[2] and these are covered with magnesite lumps of assorted

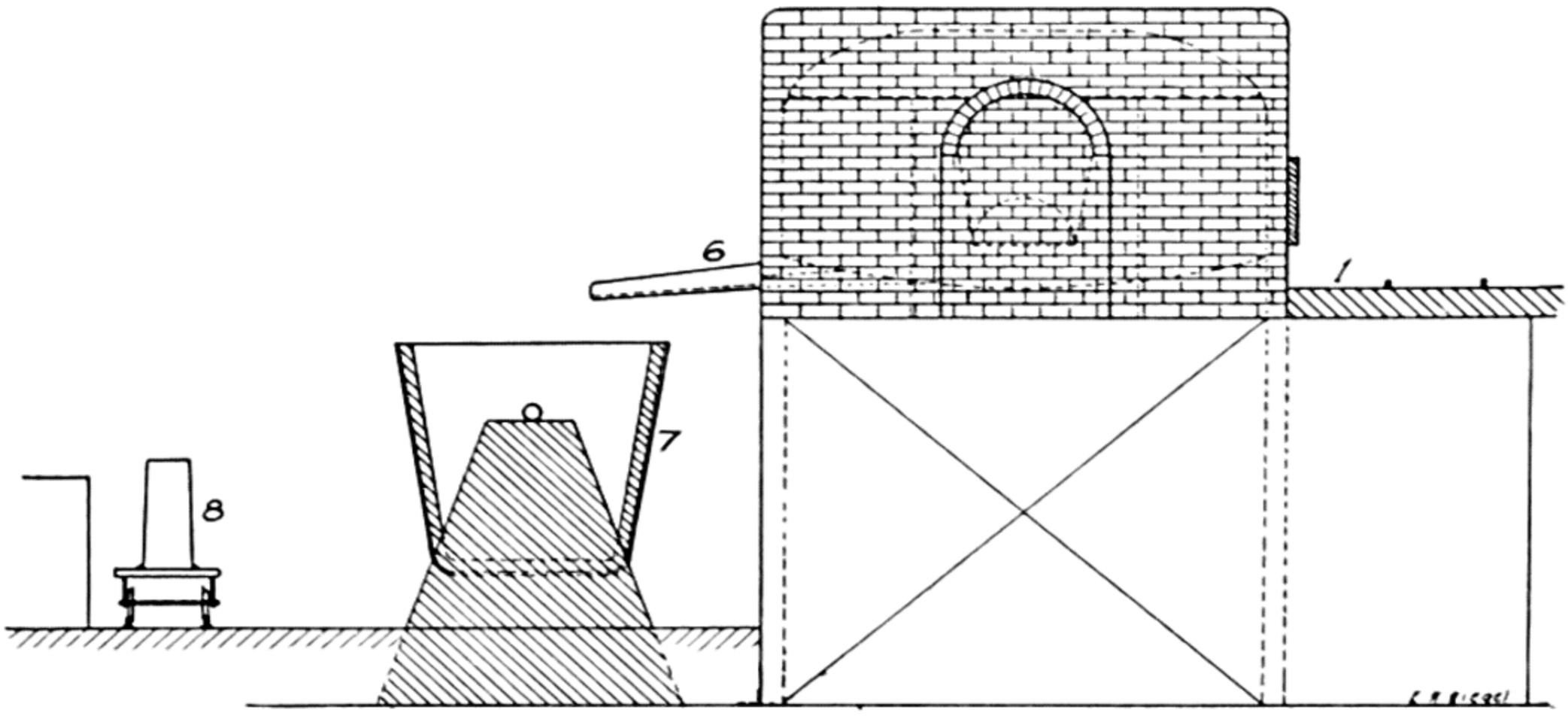


FIGURE 338.—Side view (elevation) of the open hearth furnace, showing the relative location of working floor 1; tapping trough 6; ladle 7, and ingot mold 8.

sizes mixed with 15 per cent basic slag, well burned in. The roof is lined with fire-bricks. On the floor, calcined dolomite is thrown by hand shovels before every charge, and the furnace is then ready for the run or "heat." The charge consists of

125,000	pounds of scrap iron, mainly ends of sheet steel
25,000	pounds of cold pig iron, from the storage pile
100,000	pounds of melted pig iron just from the mixer
26,000	pounds of limestone
500	pounds of fluorspar added at intervals during the 11 hours
2,000	pounds of iron ore, such as hematite

The cold materials are in narrow pans, 4 to a truck (rails). A steel housing moves on rails along the platform, and lifts each pan, pushes it into the furnace through the opened door, rotates it to dump the contents, and pulls it out again, by means of a mechanical arm with inside movable rod; the pan casting has the necessary slots to receive the arm lock. The hot pig is poured from a ladle hung from an overhead crane into a trough at one of the working doors. After all the materials have been added and have melted, the depth of the liquid metal on the hearth is about 24 inches. With the charge in the furnace, there is little to do except to reverse the gas flow and observe the progress of the reaction, until near the end of the period.

[2] 90 to 93 per cent MgO.

The relative amounts of pig and scrap vary. It may be 40 per cent pig as liquid iron, tapped for example from the mixer at the foot of the blast furnace, which holds 3 or 4 blast furnace taps, and 59 per cent scrap, with perhaps 1 per cent ore added merely in order to reduce the great amount of carbon which the pig iron brings. Or, it may be the "pig and ore process," with 70 per cent pig, 30 per cent scrap, and 12 per cent iron ore based on the metal and scrap. In this latter case, a sizable portion of the final steel come from the ore directly.

It will be well to remember that in any case a vast amount of carbon is brought to the furnace, and the essential function of the open hearth becomes the removal of any excess carbon by combustion, along with removal of phosphorus, sulfur, and silicon.

Progress of the Heat. The operator observes the appearance of the mass at the peep hole in each door, through blue glasses. The temperature is 2400° F. (1315° C.) at first, and increases to 2800° F. (1538° C.) and even 3000° F. (1649° C.); after a time, the charge is melted and the liquid appears to boil violently. A part of the boiling effect is due to the escape of gases occluded in the metal, a part to carbon dioxide escaping from the limestone, and another part to the carbon monoxide from the carbon in the pig iron, burning with the oxygen of the hematite and of the furnace gases. There are two ways for the rapid determination of the amount of carbon still present in the metal. The older way is to take a spoonful of metal and pour it into a mold to form a small pig which is quenched and then broken in two. From the appearance of the fracture, the trained eye of the operator can tell the carbon content with remarkable accuracy. The latest method is the carbometer,[2a] an instrument which measures the magnetic induction in a rod of steel cast from the metal in the furnace. With a few motions and in less than a minute, the "melter" knows the carbon content within one point (0.01 per cent C.). Besides these rapid tests, it is not infrequent to hold the furnace quiet while an analysis is made in the nearby laboratory. After 11 hours, the carbon content has been reduced to the desired point and the furnace is ready to be tapped.

Over the liquid metal there collects gradually a layer of slag, containing the impurities. Oxidized silicon and phosphorus form, with the lime from the limestone, calcium silicates and phosphates, which are melted and float on the metal, because their specific gravity is lower. The fluorspar is added to make this slag layer thinner, more readily separated from the steel.

The changes in the basic open hearth furnace are indicated in the figures below.

	Charge (Per Cent)	Steel (Per Cent)
Carbon	1.0	0.18
Silicon	1.40	.004
Phosphorus	0.05 to 2.5	.02
Manganese	1.80	.44
Sulfur	.1	.042
Iron	93.2	99.3

[2a] The carbometer is described briefly in Chapter 46. A set of curves giving carbometer readings against per cent carbon appears on p. 162, *Metals Progress*, 31, (1937).

An additional example of open hearth practice is given under "Outline of processing of heat," to show especially the rate and method of removal of carbon, as well as other particulars.

Outline of processing of heat.
Basic open hearth steel furnace in an American plant, 1941.

Analysis: Tolerances in specifications, C .63 to .67; Mn .70 to 1.00; P not over .04; S not over .040; Si .20 to .30.
Finished steel produced tested as follows:
C .65; Mn .92; P .017; S .020; Si .27.

Open hearth: Started charging 4: 50 a.m.; finished charging 6: 10 a.m.
Total time of heat 9 hours 27 minutes.

Charge: Limestone 24,000 pounds; home scrap 118,000 pounds; hot metal (pig iron from the mixer) 119,000 pounds.

"Heat finished lime" (when lime comes to the top) C was 1.19; ore added 2500 pounds
Carbon dropped as follows, and additions made as shown:

11: 08 a.m.	—1.19	
11: 45	—1.08	
11: 50	—	2000 lbs. ore
12: 20 p.m.	— .87	
12: 32	— .85	
12: 35	—	600 lbs. fluorspar, to thin the slag
12: 40	—	500 lbs. ore
12: 55	— .72	
1: 00	— .71	
1: 06	— .69	
1: 12	— .68	
1: 18	— .67	
1: 24	— .66	
1: 29	— .65	
1: 35	— .62	
1: 37	—	1200 lbs. spiegel iron for a wash
1: 44	— .61	
1: 49	— .58	
1: 50	—	1200 lbs. spiegel
1: 56	— .59	
2: 01	—	1200 lbs. silicon pig (15% Si)
2: 06	— .59	slag tested at this time, must not be too high in FeO; it tested FeO 8.49%; Fe_2O_3 6.29%
2: 07	—	2100 lbs. ferromanganese (Mn 80%)
2: 17	—	start of tap
2: 24	—	finish tap; T of steel as it run into ladle 2900° F.

Ladle additions: 0.276% Si (1200 lbs. 50% FeSi); enough aluminum to 118 tons of steel, to make 1.18 lb. per ton (bar Al).
Interval between start of tap to start of pour: 9 minutes.
Pouring ingots, into molds with hot top:
Size of nozzle 1¾ inch; pouring temperature, 2nd mold 2828° F., 20th mold 2828° F.
Soaking pit record: Surface temperature when drawn from the pit 2185° F.
Blooming and billet mills: Av. temp. of blooms leaving 44" mill 1888° F.; av. temp. of billets leaving 32" mill 1903° F.
Note: The ore is added to lower the carbon by oxidation; ore contains about 50% Fe. Carbon test by Carbometer; manganese removes sulfur.

Tapping the Furnace. A ladle with the capacity of 100 tons (15 feet high) of brick-lined steel, with nozzle in the bottom, has in the meanwhile been placed in position at the rear of the furnace. The taphole is cleared by a bar and a stream of oxygen; if the hole does not form, a small pig, red hot, is brought from the front of the furnace and placed in the taphole; a stream of oxygen is played on it and the high temperature so produced melts the cold steel and opens the hole. The steel at white heat flows out through a short trough into the casting ladle; slag runs out near the end and is run off from a side trough at the top of the ladle and forming part of it. The ladle is lifted by an overhead crane traveling in the rear of the furnaces, and carried over the ingot molds.

Casting Steel Ingots. The ingot molds are made of cast iron, open at top and bottom; they are set each on a heavy steel or copper base plate, carried on narrow trucks on rails, 6 to a truck. The bottom of the mold is formed by the heavy base plate; a little sand at the edges prevents the metal from running out. The ladle is brought over the mold, and the fire-clay plug lifted from the fire-clay nozzle in the base by a rod (with protecting fire-clay sleeve) operated from a second rod running down the side of the ladle. After one mold is filled, the plug is lowered into place, and the ladle is moved to the next. Each ingot weighs about 2½ tons, is 19 inches square (with rounded edges) and about 5 feet high.

An improvement in the casting procedure consists in placing over the top of the mold a stoneware sleeve as wide as the mold itself, and allowing the metal to rise within it. This "chimney top" does not chill the metal, allows the gases to escape, and prevents, by feeding hot molten metal downward, the large cavity formerly formed in the upper part of the ingot. A further advance is "scarfing," namely, cutting away with an acetylene torch the bad metal from the corners of the ingot.

Rimming Heat. There are to be distinguished the "rimming heat," the "killed heat," and an intermediate one, "semi-killed heat." The rimming heat may be illustrated by a manganese rimmer, a steel to be used for nuts and bolts stock. Such a steel must contain sulfur, which may be as high as 1 per cent; in this case it will be more moderate. During the progress of the melt of 100 tons, there will have been added 1000 lbs. of manganese; and while the tapping is in progress, there are added to the ladle, which takes the whole of the "heat," that is, of the tap, 300 lbs. of brimstone, 60 lbs. of anthracite to restore carbon and bring it to the required percentage, and finally 1400 lbs. of manganese in the form of 80 per cent (ferro-) manganese. The resulting steel contains, in this case, 0.16 to 0.18 per cent C, 0.55 to 0.65 per cent Mn, 0.10 to 0.12 per cent S. As the steel is poured from the ladle into the ingot molds, the liquid steel "works," that is, bubbles, for several minutes. On cooling, the ingot will be found to have a crust of close-grained metal along the outer walls, with a core of coarser grained metal, darker in color; hence the appellation "rimmed." The ingot passes through the blooming mills, and is reduced in size in other mills, undergoing continually an elongation, but never losing this composite structure of fine grained rim with coarser grain core. The purpose of the sulfur addi-

tion, and other additions in definite proportions, is to produce a steel which will give short turnings when threaded, which then fall off easily and do not plug the dies in the automatic screw-making machines. The sulfur is present in the form of manganese sulfide. The steel just described is for "hot heading" such nut and bolt stock; a somewhat different composition is selected for the "cold heading" stock, with the carbon .15 per cent and the manganese somewhat higher.

Killed Heat. A high manganese steel will illustrate the "killed steel"; such a steel might be spoken of also as a high-impact steel. The bath in the open hearth furnace is brought along in the usual way, with the addition of a certain amount of ferro-silico-manganese (66 per cent Mn, 18 per cent Si). Near the end of the period, there is added a "wash" of pan pig iron; these sink in the melt, and cause a violent action from below which drives upward any sluggish impurity which is to be slagged. Next for a "block," some 3000 lbs. of silicon-manganese iron are fed in. This addition melts and quiets the bath, giving an interval with essentially no "work," hence no change in composition; that period is utilized to make a laboratory analysis for carbon and manganese. It should be said that the quietness of this interval is helped by shutting off the gas and air. Guided by the analysis, the proper amount of 80 per cent manganese is placed in the furnace, and it is ready for tapping. To the ladle, as it fills, there may be added anthracite. The final composition is 0.30 per cent C., 1.65 to 1.75 per cent Mn, not over 0.03 per cent P, not over 0.04 per cent S. As the ladle is lifted over the ingot molds and fills these, the steel does not "work" at all; it is quiet, and begins to solidfy at once; all action in the ingot mold has been "killed." The metal is essentially uniform over a cross-section. This steel fits S.A.E. T1330.

For this high manganese "killed" steel, the hot top chimneys are used over the ingot molds.

Semi-killed steel lies between the rimmed and killed steels.

Soaking Pits. The small trucks with the filled molds are pushed under a shed in which an overhead crane travels, which carries special lifting claws fitting the mold. The claws engage the mold and lift it up, leaving the ingot (still red) standing on the platform; the mold is placed on an empty truck ready to return to the furnace building. Any mold which fails to leave its ingot is reworked in the furnace, mold and ingot. The stripped ingots are conveyed to the mill building, and first reheated to bright red heat in the "soaking pits." The pits are brick-lined chambers in the floor, 6 feet deep and 4 by 6 feet in cross-section, heated by gas. As a rule, four pits are served by one gas main.[3] The transfer of the ingots to the pits and their removal is done again by an overhead crane, carrying a grabbing tool (the dog). The reheated ingot is deposited in a steel basket on an electric truck, which carries it to the first of four or five mills, where a trip dumps the basket, so that the ingot lies on its side ready to enter between the two rolls of the mill.

[3] A sketch of the soaking pit will be found on p. 219, "The metallurgy of iron and steel," by Bradley Stoughton, New York, McGraw-Hill Book Co., 1913.

Rolling Mills. The ingot enters the first set of rolls of the mill (sometimes called the blooming mill) which reduces its thickness; it is returned to the rolls after being turned on its other side by mechanical claws, so that all four faces are pressed; it is at the same time elongated. This treatment is repeated in the next set of rolls, the steel billet lengthening at each passage while its diameter diminishes. In order to make steel rails, the rolls have grooves arranged so that two which revolve on each other leave a passage approaching the shape of the rail cross-section; the last passage has exactly the shape of the rail. The imperfect ends are cut off by heavy shears and returned to the open-hearth furnace. Each mill has two (or three) horizontal rolls, with several grooves for the smaller rolls, of gradually diminishing size; the steel may be passed back through the same rolls, forward again and back again, a number of times, each time through a smaller passage; the method of moving the steel is by smooth rollers forming the floor on which the piece rests; the floor rollers may be revolved at any speed, and may be reversed at the will of the operator, who stands at a distance on the control platform. The floor rollers as well as the mills are driven by steam engines or D. C. motors, through gears with *V*-shaped teeth. To keep the mill rolls from heating, a small stream of water is allowed to flow over them; some of it reaches the steel, but has no appreciable effect.

As the steel rail emerges from the last passage, it travels to a revolving saw which cuts its end true; it then moves on to a stop which controls its length; the saw makes another cut. A second length is measured off and cut, and the waste end sent back to the furnace. The rail, which is still red hot, is moved to a storage shed (floor rollers), where floor claws push it along resting bars toward one end of the room, to cool. One ingot of the size given makes two rail lengths, and the time required from the blooming mill to the shed is about 15 minutes.

Not only rails, but flat iron, bars, angle irons, tees, channels, and I-beams are shaped in this way. Wide flat iron (skelp) is bent and welded to form tubes (iron pipes of all sizes) by automatic operations.[4]

The process of rolling is not merely a shaping of the mass, but because of the pressure applied in the mill, the particles in the steel are pressed together, coarse particles destroyed, and the strength of the material increased.

A distinction is made between the basic open hearth and the *acid open-hearth process;* in the basic open hearth, which is the more important one, pig iron and scrap containing 2 per cent of phosphorus and even more may be used, for by the addition of lime, this phosphorus, after oxidation to its oxide, is fluxed out as calcium phosphate. The acid open hearth, the original process, makes no provision for the removal of the phosphorus; pig iron or scrap with a low phosphorus content must be used (0.045 per cent P), and the steel will contain a slightly higher percentage. The acid open hearth is used in England. Four-fifths of the rails produced in the United States are open-hearth steel.

[4] The National Tube Co., McKeesport, Pa.

Continuous Strip Mill. Increased demand for sheet steel has made a more rapid and more economical method of production desirable, and this has been realized in the Mesta machines, which roll a slab into a continuous sheet of steel at a rate not unlike the rate of paper-making on the Fourdrinier.

A slab, let us say for illustration, 35 inches wide, 13 feet long, 4½ inches thick, of low carbon steel, preheated to 2300° F. (1260° C.), is pushed (mechanically) onto rollers forming the first part of a long roller platform interrupted only by the rolling mills. From here on, the steel travels in a straight line, in one direction. The slab is fed successively to each of 4 stands called "four highs," each operated as single units and at individual speeds. Each "four high" rolling mill consists of 4 rolls, arranged vertically; reading from the bottom up, they are: an idler, a driven roll in contact with it, the gap through which the steel passes, an upper driven roll, and finally another idler, the "back-up." A scale breaker strikes the slab as it moves from the first to the second of these preliminary stands. Beyond the fourth stand, the slab reached a space called the "cooling table," where it can be moved back and forth until it has cooled to the proper temperature for the final pass, namely 1620° F. (882.2° C.). The slab is, by now, considerably elongated, and much thinner, perhaps ¾ inch. It now enters the first of a set of 6 stands, also "four highs," passing directly from one to the next and emerging from the last, with the prescribed thickness or gauge. These 6 "four highs" reduce the thickness of the steel stepwise; they have different speeds of rotation [4a] taking up exactly by the increment in speed the increment in length. The width is set by side guides. The still red sheet hurries down the long table (with driven rollers for floor), to wind itself automatically into a coil, which is pushed out and dumped onto a floor conveyor traveling at right angle to the long table.

The maximum speed on leaving the last of the 6 "four highs" is 1350 feet per minute, for the lowest thickness (.050″); the minimium speed for the heavier gauges is 200 feet. For the medium thicknesses it is around 500 feet; this means that the observer, standing on the bridge over the hot table, will see the red sheet rush by below him in 30 seconds, for a length of 250 feet,[4b] a frequent length. The time from slab to coil is 2 minutes.

The clearance at the last mill is still much greater than the thickness of the steel; for example, a clearance of .220 inches is used to produce a sheet .074 inches in thickness.

The hot mill capacity is 50,000 tons a month. The width of the sheet may be as high as 72 inches.

After cooling, the coil is passed unwound through the pickler (dilute HCl), is washed, dried, and oiled, and next *cold rolled*, with a reduction in thickness of 60 per cent. This considerable reduction is accompanied by the creation of strains, and brittleness, so that the cold rolled sheet, now cut

[4a] Thus for number 6, the final mill, 190; number 5, 160; number 4, 108; number 3, 90; number 2, 64; number 1, 46.

[4b] The length of the rolled sheet may be computed by dividing the proposed thickness in inches, into the thickness of the original slab, and multiplying by the length of the slab; width to remain the same.

in convenient lengths (a popular size is 68 inches by 120 inches), is made into piles and covered with an annealing oven. The atmosphere of the oven is controlled; the box is filled with DX gas in order to deoxidize the surface, and restore a shiny non-scale surface; the heating is indirect. After 72 hours, the pile of sheets is allowed to cool, and may then be cold rolled again, this time with no reduction (skin roll). The sheet is then inspected under a mercury arc for seams, stretcher strains, buckle, gauge and other particulars.

A part of the hot rolled steel is used as such, for the manufacture, for example, of automobile chassis frames, exhaust pipes, tubes for the differential housing.

The Bessemer Converter

Acid Process. The Bessemer converter is a pear-shaped vessel with perforations (the tuyeres) at the bottom through which a blast of cold air (pressure 25 pounds) may be introduced; molten pig iron from a mixer

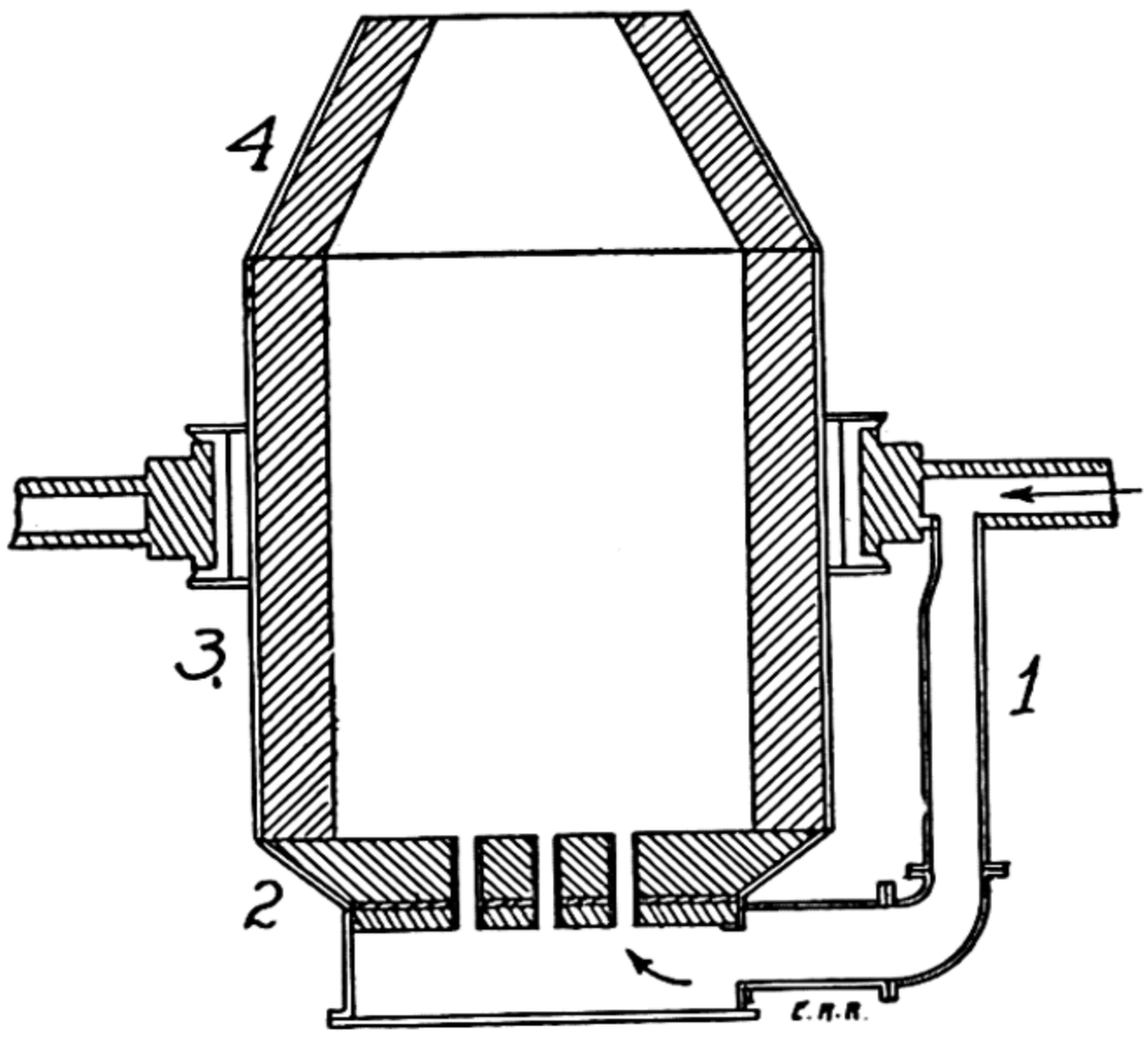


FIGURE 339.—The Bessemer converter for steel; 1, entry for air blast, cold; 2, bottom piece; 3, body; 4, nose piece of the converter. The tuyeres are shown in 2.

is poured in and blown for a period of about 20 minutes; the silicon and manganese are oxidized and combine with that portion of the iron which is oxidized at the same time. In the simplest case, that of the acid Bessemer process, three periods may be distinguished. In the first, slag forms; in the second, the liquid "boils," the carbon is burned and escapes first as dioxide, later as monoxide (CO); it is the escape of the latter gas which causes the "boil." The flame at the mouth of the converter during the second period is large. The third period is the finishing period, when the last of the carbon burns to monoxide; as its amount diminishes, the flame dies down. Much heat is produced during the blow, mainly by the burning of the silicon (*compare* Problem 2); in fact, the Bessemer conversion succeeds best when there is a 2 per cent content of silicon in the pig iron; with a lower content, 0.8 or 1 per cent, the converter must be kept hot by rapid

working. The blow over, an addition of spiegeleisen [5] is made in the converter, and a short afterblow is applied; the manganese reduces any oxide of iron which has been formed and at the same time furnishes carbon, which the main blow has practically completely removed.

A Bessemer converter for a 10-ton charge is about 15 feet high, mounted on trunnions, and elevated sufficiently to allow the pouring of the finished steel into a ladle. The converter is lined with acid (silica) bricks, and has a removable bottom piece, which lasts only 12 to 15 blows, and a removable nosepiece.[6] Other details are indicated in Figure 339. Converters large enough to hold 20 tons are not uncommon. The charge occupies only one-sixth of the space within the converter, to allow for agitation. The pig iron or melted scrap must contain not more than 0.05 per cent phosphorus.

Basic Bessemer Practice—The Thomas-Gilchrist Process. The basic Bessemer conversion differs from the acid Bessemer just described in several particulars. It is devised for phosphorus-containing pig iron, or melted scrap, and during the blow, it is the burning of the phosphorus [7] which furnishes the heat, instead of the silicon; the phosphorus content is usually 2 per cent, and may be as high as 3 per cent. Lime is added, in lump form, in order to bind the phosphorus oxide, P_2O_5, as calcium phosphate; and as such basic material as hot lime would speedily ruin the silica brick lining usually applied to the acid converter, the lining must be different, namely basic. It is made of dolomite bricks. The amount of slag formed in the basic Bessemer is greater than in the acid one, and for the same charge of metal the converter must therefore be somewhat larger. Finally, the spiegeleisen is added only after the metal is in the ladle, so that a reduction of the phosphate by the carbon in the spiegeleisen may be prevented. The basic Bessemer is much used in France and Germany, less in the United States.

The composition of the charge and of the product for the two Bessemer processes are given in Table 152.

TABLE 152.—*Composition of charge and product.*

	Basic Bessemer Process			Acid Bessemer Process		
	Charge	Steel	Undosed**	Charge	Steel	Undosed**
	Per Cent			*Per Cent*		
Carbon	3.60	0.20	(trace)	3.50	0.20	(trace)
Silicon	0.61	0.01	(0.005)	2.10	0.02	(none)
Phosphorus	2.52	0.04	(0.04)	0.04	0.045	(0.045)
Sulfur	0.07	0.05	(0.05)	0.04	0.044	(0.044)
Manganese	1.45	0.40	(0 12)	0.45	0.48	(trace)
Iron	91.75	99.30	(99.7*)	93.87	99.21	(99.8*)

* Iron oxide is present. ** That is, before correction by spiegeleisen addition.

Both steels given in the table would be mild steels for general structural purposes. The reactions are violent; the pig iron is changed to the pure iron

[5] Spiegeleisen means mirror iron; it is a low-manganese iron alloy; Mn 15%, C 4.5%, Si 0.5%, Fe 79.7%, S 0.2%, P 0.28%. The amount added is 6% of the charge, or even more.

[6] The nosepiece lasts 50 blows; the body, 200.

[7] For heat value, *compare* Problem 2.

shown under the column "Undosed"; such iron has the fatal defect that it contains iron oxide, which renders the product almost useless. The addition of the ferromanganese or spiegeleisen removes the oxide of iron, for the manganese combines with the oxygen of FeO with great rapidity; at the same time, carbon is furnished to reach the designated percentage. That the very pure undosed metal is fluid means that a very high temperature is produced in the converter.[8]

It was the invention of the use of spiegeleisen as a deoxidizer and at the same time recarburizer which saved the Bessemer process from failure in its early days (Mushet, 1856). Other deoxidizers are ferromanganese alloys with 40 to 80 per cent manganese; also silicon alloys and aluminum.

The composition of structural steel need not be those given in Table 152; in the case of the towers for the George Washington Bridge the steel used contained about 0.27 per cent silicon. The high silicon content was selected in order to improve the physical properties of the steel, not for the purpose of decreasing any possible corrosion.[9]

Slag. In the acid processes, the slag is due to the burning of the silicon, Si, to silica, SiO_2, of the manganese, Mn, to the oxide, MnO, and of some of the iron, Fe, to FeO; these react further to form manganese silicate and iron silicate:

$$MnO+SiO_2 \rightarrow MnSiO_3;\ FeO+SiO_2 \rightarrow FeSiO_3.$$

In the basic processes, the phosphorus, P, burns to the pentoxide, P_2O_5; some iron to its oxide, FeO, and the manganese again to MnO; there is then formed calcium phosphate,[10] essentially, containing iron phosphate and some manganese phosphate:

$$3CaO+P_2O_5 \rightarrow Ca_3(PO_4)_2.$$

The liquid slags are lighter than the melted steel and float on the latter.

Tilting open hearth furnaces are successfully used by a number of plants.

A continuous open-hearth process, in which 20 tons of steel are tapped at intervals from a total charge of over 100 tons, is in operation (Talbot); the main advantage is that the bottom of the furnace remains covered by the steel and is not attacked (or very little) by the slag.

Sulfur may be slagged out by means of manganese, which forms manganese sulfide, MnS.

Special Products

Nearly pure iron was made formerly from very pure raw materials, and with charcoal; it is possible to make surprisingly pure irons in the open-hearth process by holding the charge for some time longer in the furnace to lower the content of silicon and manganese; at the ladle aluminum (shot) is added liberally, perhaps 1½ pounds to the ton of iron. The Armco

[8] The purer the iron, the higher its melting point. No fuel is needed in the Bessemer conversion; as indicated before, the heat is due to the oxidation of the silicon (acid process) or the phosphorus (basic process).

[9] Private communication, The Port of New York Authority, Herbert J. Baker, engineer of steel inspection.

[10] For the use of basic slags as fertilizers *compare* Chapter 18.

brand of iron, used for cornices and conductor pipes, is such an iron; it rusts either not at all or very slowly; its composition is carbon 0.02 per cent, manganese 0.05, silicon 0.01, phosphorus 0.01.

Steel is iron containing carbon, in part as iron carbide, Fe_3C, called cementite; in part free, as graphite; the total amount for steel lies between 0.135 and 1.5 per cent C.[11] Heated and suddenly quenched, it becomes more elastic, harder, and more brittle; these qualities may be varied for any one steel by varying the temperature and the period of quenching. In

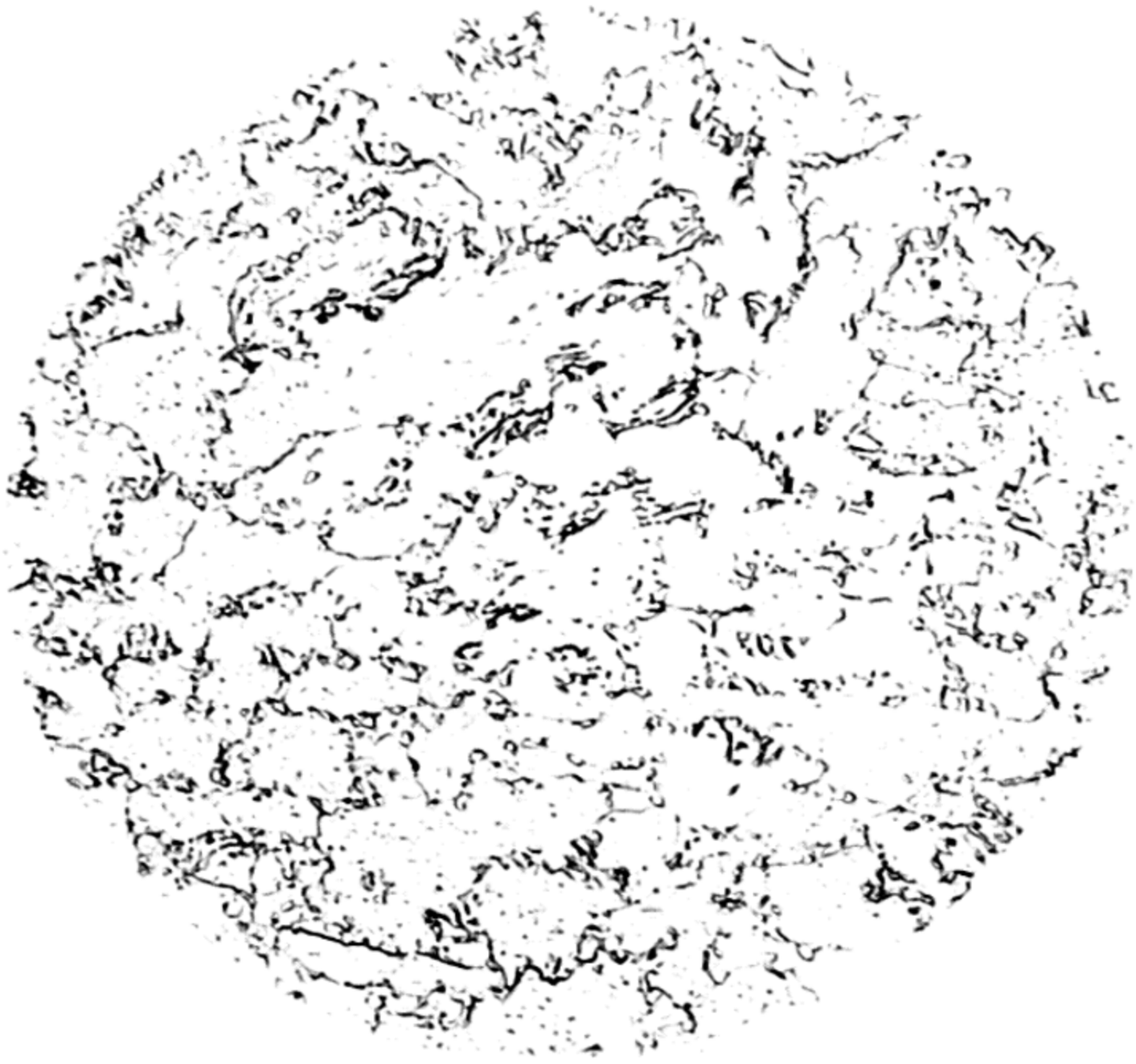


FIGURE 340.—Photomicrograph of regular plain carbon steel, containing 0.27 per cent carbon. After rolling, the steel was annealed at 1250° F. and slow cooled. The background is ferrite, and the lines and curves are spheroidized cementite. 500 diameters. (Courtesy of the Metallographic Laboratory, Bethlehem Steel Company, Buffalo, N. Y.)

low-carbon steels, most of the iron is free, and occurs as ferrite, of which there are three varieties. By heating to a predetermined temperature and cooling suddenly, the structure existing at that temperature may be preserved, with the properties which accompany it. A steel with 0.89 per cent carbon consists entirely of "pearlite," which is made up of thin parallel plates of cementite and ferrite side by side (a eutectic mixture); above 0.89 per cent carbon, there is a network of cementite around pearlite beads; below 0.89 per cent, ferrite is mixed with pearlite. "Austenite" is a solid solution of carbon in γ-ferrite. The structure of the steel may be studied by means of the metallographic microscope (see illustrations).

Steel is made into a number of forms suitable for certain uses. Several are given in the following list, which has also the quantity in thousands

[11] Iron with 2.5% carbon and more is pig iron.

of long tons for the year 1939 [12] (U. S.); rails 1175; track accessories 462; structural shapes 2245; bars: carbon steel 2509, stainless steel 20, other alloy steels 672; concrete bars 1094; plate 2819; sheet: plain and black, 2819; strips: plain 748, stainless 33, other 630; skelp 1941; total finished steel 48,132.

In ordinary steels the impurities also affect the properties; manganese makes the steel more elastic, hence more resistant to a shearing force. Chromium or tungsten raise the tensile strength; and chromium steel resists shocks better than mere carbon steel.

Extra-hard steel may contain carbon only, or manganese 0.5 to 2 per cent with carbon 0.5 per cent and less; or 1 per cent tungsten with 0.5 per cent carbon; or chromium 1 per cent again with carbon 0.5 per cent.

Gun barrels [13] are made of chrome steel (1 or 2 per cent) (U. S.); armor plate for battleships (12 in. thick) is nickel-chrome steel (3.3 per cent Ni, 1 per cent Cr), case-hardened. Nickel steel (with 25 per cent Ni) is made in crucibles; the melted steel and melted nickel are poured together into a larger receiver. Nickel raises the tenacity without changing the elastic limit; vanadium has the same effect as nickel and only one-fifth as much is needed. A nickel steel with 3 per cent Ni, 0.40 C, 0.1 Si, 0.60 Mn, deoxidized by aluminum, possesses after heat treatment a tensile strength of 300,000 pounds per square inch; it is ductile and tough. Zirconium, molybdenum, and other elements are also used to strengthen steel.

Castings made of steel are presented in Chapter 45. An open hearth furnace producing steel for castings may be charged as follows: pig iron, 6,000 lbs.; heavy melt steel scrap, 22,500 lbs.; malleable iron, 1,600 lbs.; spring steel, 2,000 lbs.; home scrap, 8,200 lbs.; iron ore, 400 lbs.; coke, 200 lbs.; pebble lime, 2,400 lbs.; dolomite, 1,400 lbs.; fluorspar, 300 lbs. Later, ferro-manganese and ferro-silicon iron are added. The tap is 20 tons.

Self-hardening tool steel, one of the most striking as well as important discoveries,[14] contains chromium 2 per cent, tungsten 8.5 per cent, carbon 1.85 per cent, manganese 0.15 per cent, silicon 0.15 per cent, phosphorus 0.025 per cent and sulfur 0.030 per cent. It is heated to 940° C., then cooled in a bath of molten lead, and after that, in the air; it is used for cutting tools in the machine shops, and retains its edge even though red hot from the friction of the cutting. Other high-speed tool steels in the past have been high-tungsten steels; for example, the 18-4-1 grade contained 18% W, 4% Cr, 1% Va., 0.5% Mn, between 0.40 and 0.80% C, balance iron. The effort in the past 12 years has been to substitute molybdenum for the rare and expensive tungsten, and this has been successful. Such a molybdenum high-speed tool steel is the following: 0.80% C, 1.50% W, 4.00% Cr, Va. 1.00%, Mo 9.00%, balance iron.

Columbium in Stainless Steels. Several iron alloys are briefly discussed in Chapter 45, among them stainless steels, which are precious to

[12] Corresponding figures for more recent years not available.

[13] A 14-inch (bore) gun consists of gun proper, inner tube, jacket, hoops and breech-lock pieces; it requires about 2 years to manufacture; it is about 40 feet long. The smaller guns up to 3 inches have tube, inner tube, jacket, and breech-lock. The jacket is forced while hot over the tube (shrunk on).

[14] By Taylor and White, of the Bethlehem Steel Co.

the chemical engineer because they resist corrosion. When stainless steels are subjected to heat, they become susceptible to corrosive chemicals. A way to preserve the non-corrosive property of the stainless steel consists in adding columbium (F. M. Becket); the columbium [15] combines with the carbon in the steel, and the resulting carbide remains dissolved in the ferrite, in the straight chromium stainless steels, or in the metal, for such alloys as 18-8. The difficulty is thought to have been that chromium carbide formed a carbide which segregated. The amount of columbium added, in

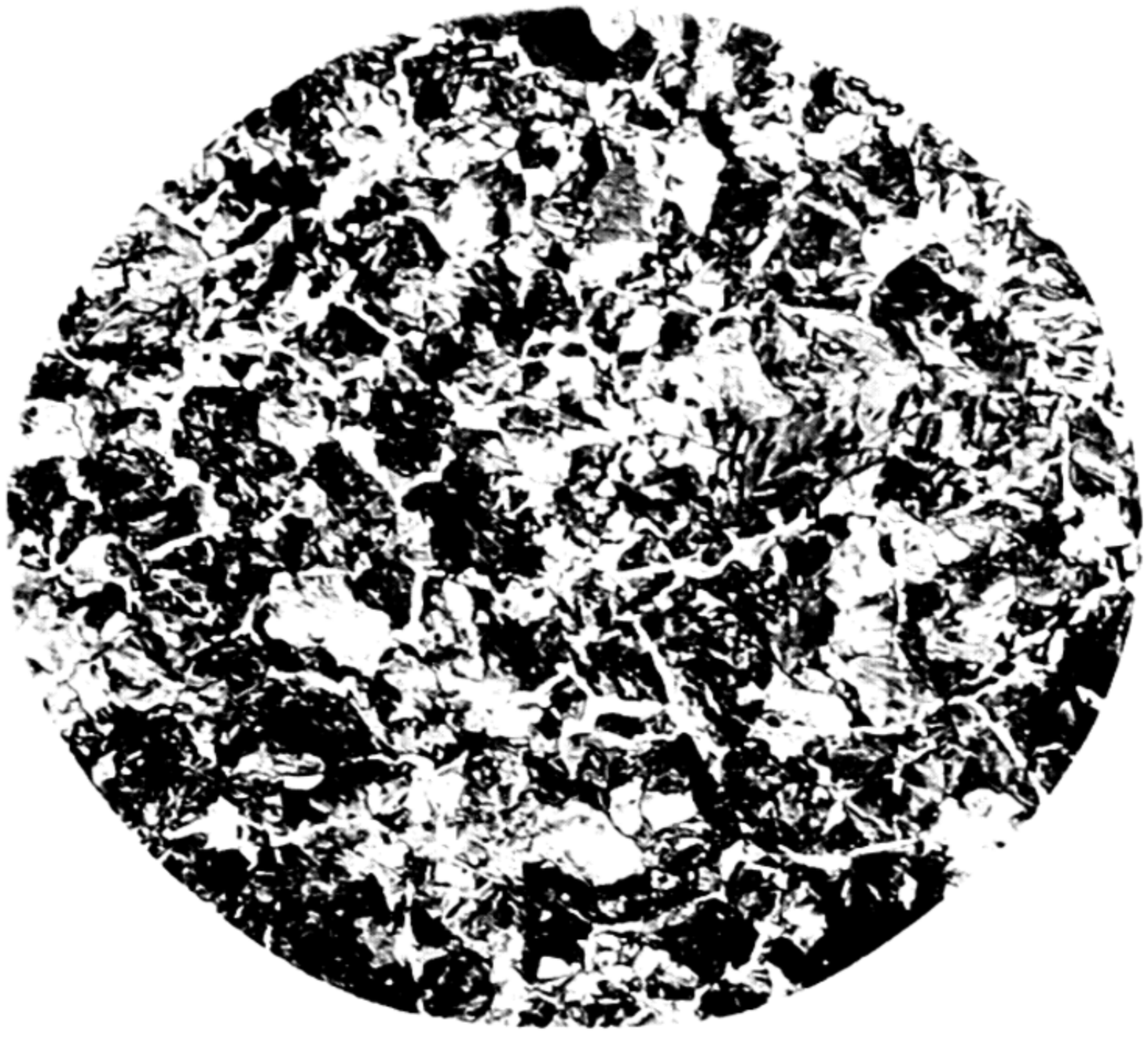


FIGURE 341.—Photomicrograph of a nickel-chrome steel after rolling. The steel contains C .39, Mn .68, P .015, S .018, Si .20, Ni 1.22, Cr .57. The dark areas are pearlite, the white network is due to ferrite. 100 diameters. (Courtesy of the Metallographic Laboratory, Bethlehem Steel Company, Buffalo, N. Y.)

the form of ferro-columbium, is about five times its carbon content; to be effective, the carbon content must not be over 0.02 per cent.

Heat Treating. Fundamental to heat treatment is the iron-carbon phase equilibrium diagram, on which temperatures against composition are plotted, and the critical temperature phenomena. To take the latter first: When a piece of carbon steel is heated at a regular rate, it expands continuously until 1350° F. is reached (for a given composition), when it not only no longer expands, but actually shrinks, although the temperature is still rising. By the time the temperature has reached 1475° F., the piece expands again. On cooling the same steel from a high temperature (such as 2600° F.), there is a gradual contraction until 1375° F. is reached, when it stops shrinking, and expands slightly; on continued cooling, at 1225°

[15] For source and method of extraction *see* Chapter 49.

F., the contraction is resumed. This range is called the critical range, and here it lies between 1225 and 1475° F. The equilibrium diagram marks the limits for the several phases. (Compare the earlier section "special products.")

The critical range differs somewhat for the various steels. All heat-treating operations must have regard for the critical range of the specimen.

The various types of heat treating are: 1. Annealing, which means heating above the critical point and holding it there for 24 to 72 hours, then cooling slowly while covered. 2. Normalizing, which is the same as annealing, except that the steel is allowed to cool in air, which is also faster.

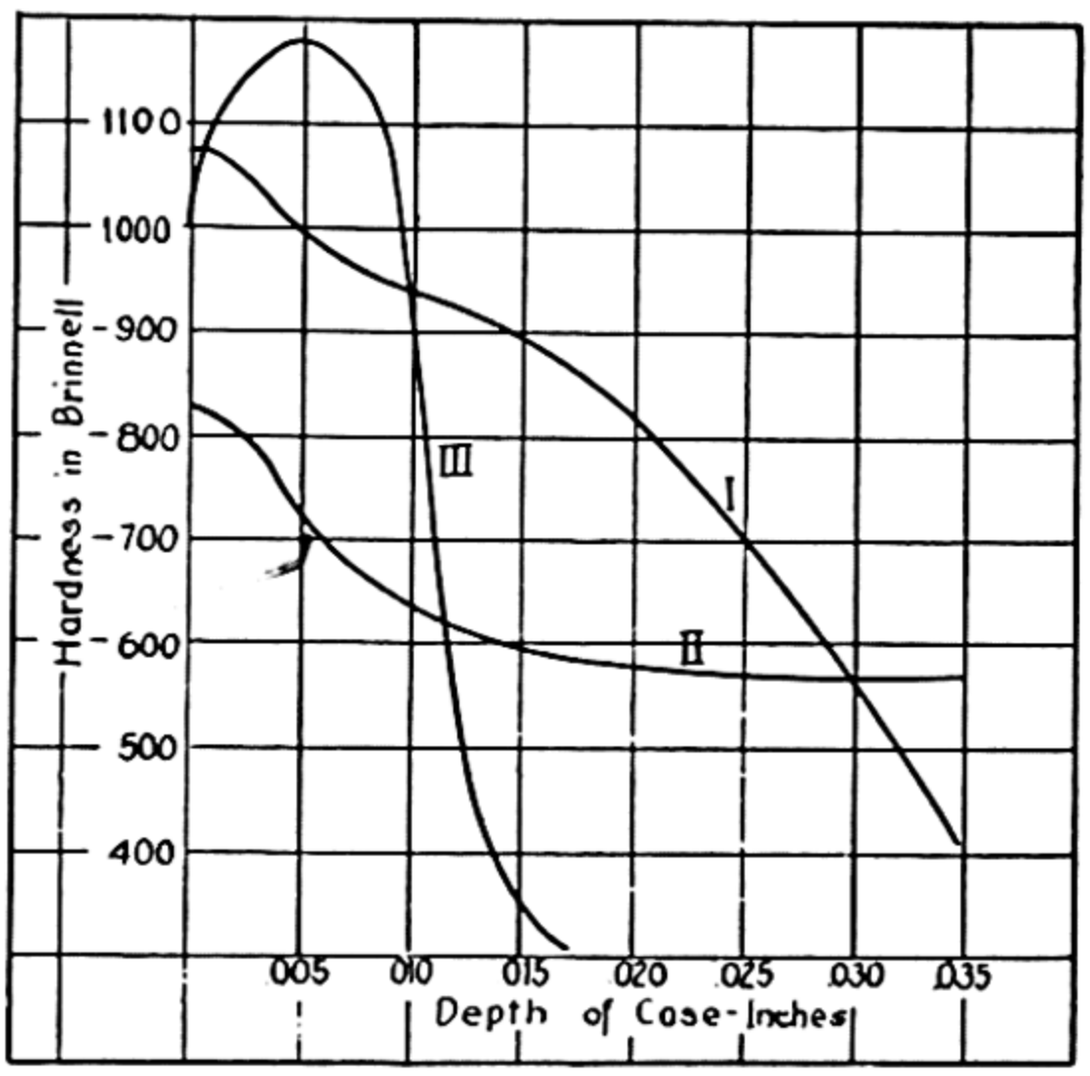


FIGURE 342.—Comparing nitrided steel and carburized steel. I, Cr-Al-Mo steel, nitrided; II, Ni-Mo steel, carburized; III, Cr-Mo steel, nitrided. (From *Metals and Alloys*.)

3. Quenching or hardening; that is, plunging the steel heated to above its critical point, into a 10 per cent salt solution, or into water, for rapid cooling; or into oil, for medium rapid cooling. Some steels having a high alloy content can be cooled in air. The process of quenching preserves the structure as it is at the high temperature; it produces a high degree of hardness. 4. Tempering, or better, "drawing," which means heating the hardened (quenched) steel to a certain temperature which must not in any case equal or exceed the critical point, and holding it there for some time. Drawing moderates the great hardness produced by quenching, and restores some of the original ductility. Example: A .45 per cent carbon steel quenched in water has 600 Brinell hardness; it is heated at 800° F. (427° C.) for one hour per each inch of thickness. The resulting steel has a 444 Brinell hardness. For ordinary work, these drawing temperatures range from 500° F. to 1200° F. (260° to 649° C.).

Several classes of carbon steels, which make up 85 to 90 per cent of heat treated steels, are distinguished, and their susceptibilities to heat treatment differ. Steel with carbon from .03 to .10 per cent (3 point to 10 point) is used for sheets, chain steel, angle iron, and is not heat treated; neither is the next class, .10 to .30 per cent carbon steels, which comprise structural steel and steel which will be case-hardened. Steel with .30 to

.60 per cent carbon is the forging grade; it is made into automobile crankshafts, wrenches, and it is heat treated. (Generally, steel with carbon over .40 is for heat treating purposes.) The next class, .60 to .80 per cent carbon steels are for dies, chisels, punches and rails, and is not heat treated;

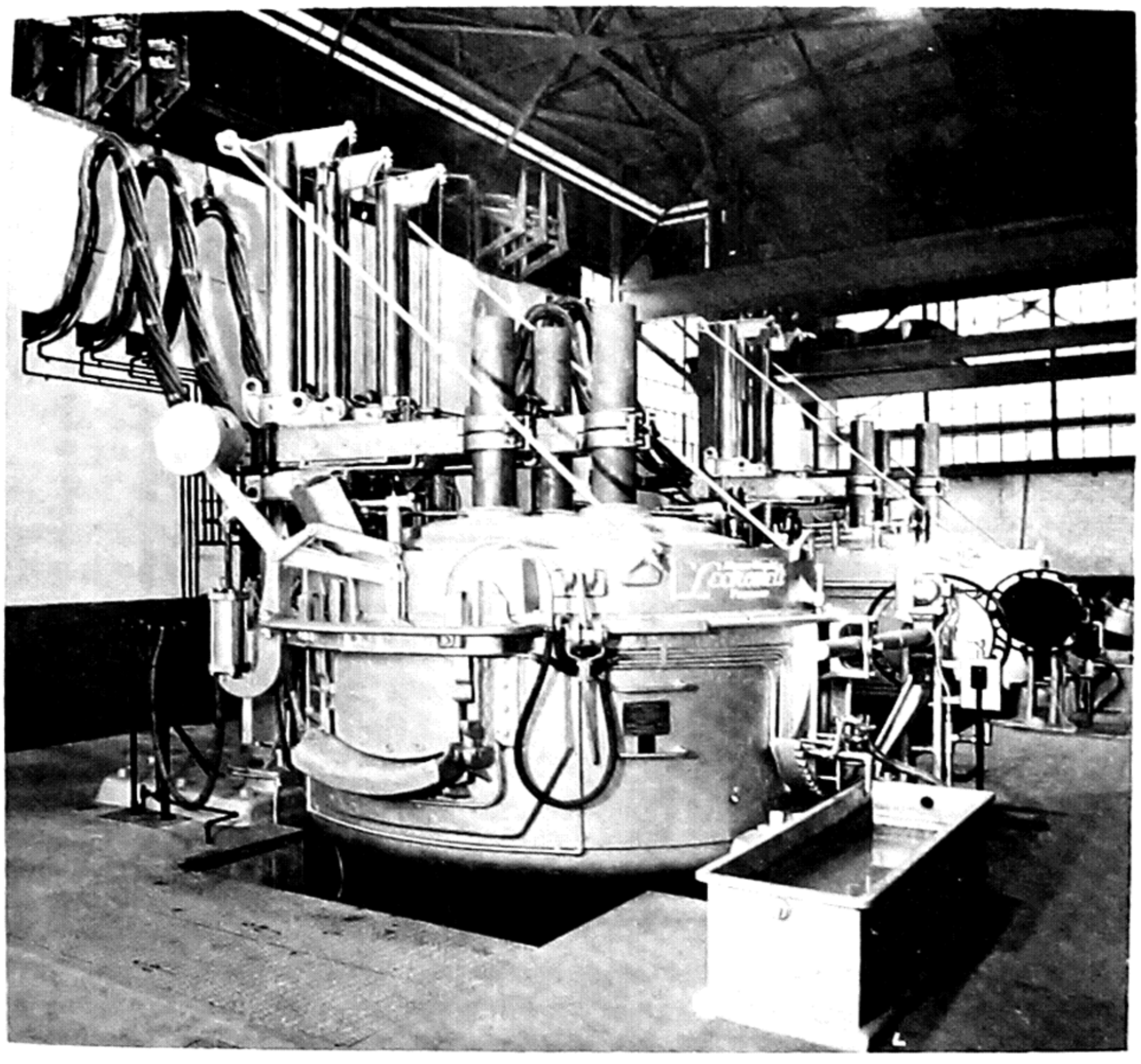


FIGURE 343.—Two Lectromelt furnaces, each of three-ton per hour capacity, of the top charge type. When the charge is finished and ready to pour, the furnace is tilted, and the metal run into ladles. The furnace is righted, the electrodes are lifted, anchoring bolts opened, and the top of the furnace rotated to the left of the reader, exposing the whole of the interior, for easy charging of the next batch. (Furnished by the Pittsburgh Lectromelt Furnace Corporation, Pittsburgh.)

while the following one, .90 to 1.05 per cent carbon, for automobile springs, is oil quenched and heat treated. File steel is 1.15 to 1.30 per cent carbon and is extremely hard.

Case-Hardening. In order to harden the surface while the interior remains soft and tough, steel may be enclosed in a thin case of carbon-rich metal, by heating it while packed in carbonaceous materials. Powdered bone, wood charcoal, charred leather, graphite, anthracite, lampblack, potassium cyanide (fused), sodium cyanide (fused), potassium ferrocyanide, acetylene, propane and other substances are used. The heating is out of

contact with the air. The carbon of the packing slowly penetrates into the steel (nickel-steel automobile gears are case-hardened to a depth of 0.040 inch); the steel is usually cooled to a black heat, reheated to a high temperature, and then quenched, in order to temper the case. Balls for bearings are case-hardened, also cams, knives for weighing scales, gears of all kinds, rifle barrels and many other objects. 98 per cent of case-hardened steels are treated as just described.

Case-hardening is also accomplished by nitriding, or by a combination of nitriding and carburizing. Nitriding alone is done with ammonia gas in air-tight containers, at elevated temperatures, and with steels of special composition. Case-hardening in a cyanide bath brings about both carburizing and nitriding; sodium cyanide or potassium cyanide is always diluted with salt or other inert material, in order to moderate the action.

Crucible Steel, Electric Furnace Steel

In the cementation process, iron bars of high purity were packed in charcoal, enclosed in a box, and heated for periods of many days. After cooling (also several days), the bars were unpacked and worked in variety of mechanical ways in order to make them homogeneous. The product was a high carbon steel, at that time the hardest (after suitable tempering) steel available. This lengthy process was superseded by the crucible process, in which a steel of uniform composition could be made in less time. Melting the steel offered the additional advantage that additions other than carbon could be made, such as other metals, which had the property of hardening steel. The crucibles have in turn been displaced by the electric furnace, which may be considered rather a large crucible in which heat is applied directly to the charge, by the conversion of electrical energy to heat, and need not pass through the walls of the crucible.[16]

The capacity of the steel furnace is not large; it runs from 1200 pounds to as much as 6000 pounds (tool steel) at one pour. A coreless induction furnace has been found well adapted to melting cobalt high-speed steel, tungsten high-speed steel, heat-resisting alloys, corrosion-resisting alloys and special compositions for tool and magnet steel. A number of special alloys are listed in Chapter 45.

The materials charged are selected scrap, flux, deoxidizers, muck bar (a very pure steel), ferro-tungsten, for example, and other alloys.

It is essential to make a distinction between structural steel and crucible steel; the former is made in huge quantities, and sells under 10 cents a pound, while the latter is made in small lots, and brings 80 cents a pound.

Ferro-Alloys. A number of ferro-alloys are made in considerable quantities. Ferro-manganese and its lower grade, spiegeleisen, are made in the blast furnace from manganese-bearing ores. The stronger grades of ferro-silicon, perhaps the most important ferro-alloy, are made in the electric furnace; ferrochrome, ferrotungsten, and ferromolybdenum also. The lower

[16] The Stassano, Keller, Girod, and Heroult furnaces are discussed in *Electrochem. Met. Ind.*, 7, 255 (1909), with illustrations. *See also* Chapter 4 on the steel furnace, in "The steel foundry," J. F. Hall, New York, McGraw-Hill Book Co., 1922.

grades of ferrosilicon, up to 10 per cent, are made in the blast furnace, by increasing the coke ratio. Ferrovanadium is made in the electric furnace; ferrotitanium is made to some extent by the thermite process, but mainly in the electric furnace.[17]

The production of ferro-alloys in 1946 was 1,480,975 net tons, of which ferrosilicon accounted for 614,422 tons and ferromanganese for 491,973 tons. The "value" of the amount shipped indicates an average price of $111.8 a ton.

The relative importance of the various processes and annual capacity of steel manufacturing facilities are shown in the table below.

TABLE 153.—*Steel capacity, and steel production by processes, in net tons.**

	Annual capacity on Dec. 31	Open hearth	Bessemer	Crucible	Electric and all other	Total production	Per cent total capacity
1944†	93,564,560	80,363,953	5,039,923	25	4,237,699	89,641,600	95.8
1946	91,890,560	60,711,963	3,327,737		2,563,024	66,602,724	72.5

* Minerals Yearbook.
† The year with highest total production since 1942.

In 1947, steel billets (Pittsburgh) were quoted at $39 to $42 a ton, over the year; in 1948, between a low of $45 and $58.24; in 1949, February, the latter price still held.

OTHER PATENT

U. S. Patent 1,786,322, electric furnace for melting metal.

PROBLEMS

1. A charge of metal for a basic open hearth furnace weighs 225,000 pounds and contains 1.4 per cent silicon; the metal tapped weighs 200,000 pounds and contains 0.004 per cent Si. All the silicon has formed calcium silicate $CaSiO_3$. How much calcium silicate is obtained?

The corresponding figures for phosphorus are 0.1 per cent in the charge and 0.02 per cent in the metal; calcium phosphate is formed, $Ca_3(PO_4)_2$. How much? In the acid open hearth, no lime is added; the silica forms iron silicate with the iron oxide, FeO; using the figures given above for silicon, and assuming enough ferrous oxide to be formed, how many pounds of iron silicate would be formed?

2. A 10-ton charge in a Bessemer converter has the composition given below: C 3.50 per cent; Si 2.10; P 0.04; S 0.044; Mn 0.48. Right after the blow, before any addition is made, the steel contains no carbon, no silicon, no manganese, while the phosphorus and sulfur content are unchanged. From the heats of combustion below, compute the number of B.t.u. evolved; and comparing Chapter 12, find the weight of coal which would be equivalent to this amount of heat.

1	pound	of	silicon	on burning to	SiO_3	evolves	12,700 B.t.u.
1	"	"	phosphorus	" " "	P_2O_5	"	10,700 "
1	"	"	manganese	" " "	MnO	"	3,000 "
1	"	"	carbon	" " "	CO	"	4,409 "

NOTE: For other problems consult "Metallurgical calculations," in 2 vols. by Joseph W. Richards, New York, McGraw-Hill Book Co., 1910; steel problems are in vol. 2.

[17] "The ferro-alloys," J. W. Richards, *Ind. Eng. Chem.*, 10, 851 (1918). An up-to-date discussion of ferro-alloys will be found in the chapter on "Metals and Ferro-alloys used in the manufacture of Steel," by W. J. Priestley, pp. 615-621, in "Metals Handbook," 1936 ed., Cleveland, O. Read also "Ferroalloys" in Steel Products Manual, Section 1, p. 27, June 1, 1941, Amer. Iron and Steel Inst., N. Y. 1, N. Y.

Reading References

"The steel foundry," John Howe Hall, New York, McGraw-Hill Book Co., 1922.

"The metallography and heat treatment of iron and steel," Albert Sauveur, Cambridge, Mass., Sauveur and Boylston, 1916.

"Story of steel," J. B. Walker, New York, Harper Bros., 1926.

"Principles of the metallurgy of ferrous metals," Leon Cammen, New York, *Am. Soc. Mech. Eng.*, 1928.

"Index to iron and steel patents," V. E. Kinsey and T. E. Hopkins, Pittsburgh, American Compilation Co., 1931.

"Sheet steel and tin plate," R. W. Shannon, New York, Chemical Catalog Co., Inc., (Reinhold Publishing Corporation), 1930.

"Equipment of modern X-ray laboratory for the study of steel," G. L. Clark, *Ind. Eng. Chem.*, 20, 1386 (1928).

"On nitriding: symposium of 1929," supplement to *Trans. Soc. Steel Treating*, 16 (1929), 222 pages.

"The nitriding of iron and its alloys, I—Ammonia dissociation and nitrogen absorption in the nitriding process," A. W. Coffman, *Ind. Eng. Chem.*, 24, 751 (1932); "II—Observations on case properties of nitrided iron and its alloys," *ibid.*, p. 849, with 24 micrographs.

"Nitriding," V. O. Homerberg, *Iron Age* (October 15, 1936).

"The manufacture of plain carbon steel in top charge rapid type furnace," W. B. Wallis, *Trans. Electrochem. Soc.*, 68, 43 (1935).

"Some aspects of steel chemistry," John Johnston, *Ind. Eng. Chem.*, 28, 1417 (1936).

"The reaction processes in the basic open-hearth furnace," G. Leiber, *Mitt. Kaiser Wilhelm Inst. Eisenforch. Düsseldorf*, 18, No. 10, 34 (1936); quoted through *C. A.* 31, 639 (1937).

"Recent developments in open hearth furnace; design and operation," L. F. Reinartz, *Mining Met.*, 17, 296 (1936).

"Columbium, from a laboratory curiosity to a widely used commercial product," James H. Critchett, *Trans. Electrochem. Soc.*, 69, 63 (1936).

"Some factors influencing segregation and solidification in steel ingots," Leon T. Nelson, *Am. Ins. Min. Metall. Eng. Techn. Publ.* 802 (1937).

"New carbometer controls speeds production and improves quality," Gilbert Soler, *Metal Progress*, publ. by Amer. Soc. for Metals, 31, 159 (1937).

Perkins medal address, Frederick M. Becket, *Ind. Eng. Chem.*, 16, 197 (1924); a valuable general article on ferro-metals.

"The mechanical properties of some austenitic stainless steels at low temperatures," E. W. Colbeck and W. R. D. Manning, *Trans. Inst. Chem. Eng. (London)*, 11, 89 (1933).

The iron-carbon-temperature diagram will be found on p. 140, in "The Phase Rule," Alexander Findlay, London and New York, Longmans, Green and Co., 1927, or on p. 253 in the "Metals Handbook" for 1936, or on p. 438 in "The metallography and heat treatment of iron and steel," Albert Sauveur, Cambridge, Mass, Sauveur and Boylston, 1916.

"Metals Handbook," 1936 edition, American Society for Metals, 7016 Euclid Avenue, Cleveland, Ohio.

"High strength cast steels," George Delbart, *Trans. Am. Foundrymen's Assoc.*, 47, 179-194 (1939), the translation of a French article.

"The working, heat treating, and welding of steel," supplemented with a series of laboratory assignments, Harry L. Campbell, New York, John Wiley and Sons, 1940.

"Ingot phase of steel production," Emil Gattham, Baltimore, Gattham Engineering Corporation.

The study of metals involves the application of several sciences. The extraction of the metals from their ores, and the finding of the ores, is the task of metallurgy. In explaining the origin of the ores, metallurgy leans on geology; in choosing the reactions for the extraction and refining of the metals, the metallurgist applies chemical science. An important branch of metallurgy is metallography, the study of the internal structure of metals and alloys.

Chapter 49

Copper, Lead, Zinc, Tin, Mercury

The metals copper, lead, zinc, tin, and mercury form a middle group of metals, more expensive than steel and iron, but cheaper than the precious metals. They may be described as base metals, because they are relatively easy of attack by acids and reagents, and because they form the oxide when heated in a blast of air. The precious metals remain unaffected under such conditions; in fact, silver is rid of lead by oxidizing the latter. The relative importance of copper, zinc, and lead is shown by the table below,[1] which also indicates what portion of the metals are produced in the United States. Mercury is less important and will be treated separately; nickel and tin are discussed further on:

TABLE 154.—*Production of copper, lead and zinc U. S. and world, in short tons.**

	1943 (U. S.)	1946 (U. S.)	1943 World	1946 World
Total new copper	1,090,818	608,737	3,038,000	2,023,000
Total new and old copper	1,814,451	1,290,185		
Primary zinc	942,309	728,262	2,017,800	1,550,400
Primary and redistilled secondary zinc	990,524	772,778		
Primary lead	469,612	338,197	1,736,000	1,285,300
Primary and secondary lead	811,706	730,984		

* Minerals Yearbook. The world figures are for smelter production, the U. S. figures for mine production.

Primary lead production in 1947 was 455,000 short tons, secondary lead 504,000 tons, while for zinc, for the same year, primary metal totalled 806,100 tons, secondary 56,100 tons.

It will be noted that for each metal, a considerable part comes from the United States; the proportion is likely to remain the same in the future except for copper, which may be produced extensively in Africa. The production of mercury is decreasing in the United States and Mexico, while the Italian and Spanish productions have maintained their lead. The nickel refined in the United States is chiefly from Canadian ores, while the tin is from ore shipped in from Bolivia, Netherland East Indies, Congo.

Compared with pig iron, these productions are small, but the uses of these metals are so specific that it would be difficult to do without them. It is interesting to note that copper serves to transmit[2] the electrical current, and to collect it at the generator; zinc serves in dry cells; while lead is the

[1] Data in the tables in this chapter and the next are from Minerals Yearbook, 1946, published by the Bureau of Mines, Department of the Interior.

[2] Aluminum is well suited for power transmission.

metal used in storage batteries; hence all three are closely connected with electrical practice. Other uses of the metals and their alloys will be found at the end of the chapter.

Copper

Copper, the red metal, occurs in the native form only in the Upper Peninsula of Michigan; the shafts are deep (5000 and 6000 feet). A number of blocks of the metal have been found which are so large that they cannot be brought to the surface through the shaft; and they cannot be dynamited to smaller fragments because the metal is soft enough to yield, preventing fracture. Other copper fields have combined copper, mainly as sulfides, but also as carbonates and silicates. Examples are chalcopyrite, $Cu_2S \cdot Fe_2S_3$; bornite (peacock ore), $3Cu_2S \cdot Fe_2S_3$, richer in copper (55 per cent); chalcacite, Cu_2S, with 80 per cent copper; azurite, and malachite,[3] $CuCO_3 \cdot Cu(OH)_2$, carbonates; chrysocolla, a silicate. Malachite is of an intense green color; azurite and chrysocolla are blue. When the ore occurs in veins, a high-grade material is obtained, with 8 to 12 per cent Cu; but low-grade ores are also profitably mined and worked to as low a content as 1 per cent. The principal producing countries are indicated in the table below:

Table 155.—*Copper production in metric tons (Smelter).**

	1943	1946
United States	1,103,918	592,229
Chile	489,320	358,603
Africa	434,027	356,030
Canada	232,740	151,499
U.S.S.R.	130,000	—
Japan	119,858	—
Mexico	43,013	52,373
Germany	31,300	19,050
Yugoslavia	32,000	—
Peru	28,215	19,703
Australia	20,785	19,104
Belgium	18,320	—
Sweden	15,938	16,385
Finland	15,535	18,960
(All Europe)	(258,676)	—
(All Asia)	(141,470)	—
World	2,756,195	1,835,000

* Minerals Yearbook. The world total includes estimates for the unreporting countries. Smelter figures are somewhat lower than mine production figures.

Within the United States, the production in 1946 in the several states would allow the following order, for tonnage produced: Arizona 48 per cent; Utah, 17.1 per cent; Montana, 9.65 per cent; New Mexico, 8.3 per cent; Nevada, 8.0 per cent; Michigan, 3.57 per cent; Tennessee, 2.12 per cent.

The Montana ores (Anaconda) are high-grade sulfides; in the Miami district in Arizona, the ores are low-grade sulfides. Nevada (Ajo) has azurite and malachite, and the mines are of the open pit type. Some of the

[3] The Egyptians used malachite for carvings.

Arizona copper mines are shaft mines, and others open pit mines (Jerome); Bingham in Utah is an open pit mine.

Concentration of the Ore. The high-grade sulfide ore, with 2 to 8 per cent copper, is concentrated by floating off the lighter earth and rock with flowing water, in classifiers such as the Dorr, in jigs, or on shaking tables with grooves; the jigs are the older devices and are being displaced by the classifiers. A preliminary crushing gives the desired size. For low-grade ores, the crushing in jaw crusher [4] or gyratories [4] is followed by pulverizing in ball mills [4] to pass (90 per cent) through a 40-mesh screen. After screening, the fine material sometimes receives the "coating oil," with which it is intimately mixed; the oiled powder next passes to the flotation machines, with either paddle or air agitation. More generally, the ore receives no preliminary oil treatment. The flotation machine contains the "frothing oil" suspended in water; the emulsion so formed has a selective action on the crushed ore; the sulfides are lifted into the froth, while the worthless material sinks. The lifting is done by a bubble of air which adheres to the oil-moistened particle and carries it up. The froth overflows to rotary suction filters which deliver a cake of concentrated ore, dry enough to be sent to the smelter. The flotation machine is small, and batteries consisting of many units are used.

The oil which serves for flotation is usually creosote oil. The amount is surprisingly small, perhaps one quart to a ton of ore. Besides the creosote oil, pine oil, certain coal-tar oils, kerosine acid sludge from the refineries, and a few others, are suitable. Mineral salts and organic substances are also added, with the oil.

Without the flotation system, it is doubtful if low-grade ores could be profitably extracted.

Smelting of the Concentrated Sulfide Ore to Crude Copper. The concentrated ore is placed on the hearth of a reverberatory furnace [5] and heated with free access of air. Sometimes the ore is first melted and cast into pigs, and these fed to the furnace. As the melting progresses, a part of the sulfide becomes oxidized, and the oxide acts on unchanged sulfide, liberating the metal and forming sulfur dioxide gas. The mass has melted by this time, and the metal sinks to the hearth; it is tapped at intervals. A flux is added in order to bind siliceous admixtures, and the slag which forms lies at the surface. The reaction between the oxide and the sulfide is violent and audible:

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2.$$

The product of this operation is crude copper, called blister copper, because it has cavities due to escaping gases. The blister copper is cast into anode sheets for the electrolytic refining. Blister copper is about 98 per cent Cu; it retain any gold or silver which the ore contained.

There is another way to make crude or blister copper, consisting of two steps. First the ore is charged into the rectangular blast furnace (24 or 30 feet long, 4 feet wide) with coke and flux, and there melted; the

[4] Chapter 44.
[5] Chapter 4.

copper sulfide remains sulfide, but the gangue is removed as a slag, so that the result is really a purification of the copper sulfide, now called the "matte." It is tapped at intervals, and used while still hot in the next step, the Bessemer converter. The slag is also tapped at a special taphole.

The hot melted sulfide is fed to a small converter (1 to 3 tons) resembling the Bessemer for steel [6] with, however, an important difference: the tuyeres are in the side of the converter, high enough so that the metal formed drops below them and escapes the oxodizing action of the blast. A small amount of acid flux is added, and the blowing performed. Sulfur dioxide escapes, and the metal sinks below the tuyeres; as the heat evolved is not so high as in the steel converter, the metal is less fluid, and this construction prevents the choking of the tuyeres. The converter is discharged by tipping. The iron impurities are oxidized and form silicates with the acid lining of the converter, or with the flux.

The tendency is to combine the two steps, blast furnace followed by the converter, into one, by melting in the converter itself (horizontal cylinder) and then blowing the melted sulfide.

Certain ores are adapted for treatment by the two-stage pyritic method, in which a saving of fuel is affected by using the heat of combustion of the iron pyrite which they must contain; a copper matte is produced which is made into blister copper in one of the ways described above.

There are many variations in the smelting of copper sulfide ores; in many cases a preliminary burning off of much of the sulfur, called roasting, is a separate process. It is performed in rotary shelf burners, similar to the Herreshoff furnace described in Chapter 1; or in the Dwight-Lloyd sintering machine, in which an endless belt made of cast-iron buckets with perforated bottoms pass over a strong suction box after their ore contents have been ignited by an oil flame.

Wet Methods of Extraction. The methods just given apply to sulfide ores only. Azurite and malachite may be extracted by the sulfuric acid-leaching process; a solution of copper sulfate results from which the copper is precipitated partly by electrolysis, the rest in powder form by old iron (Ajo district in Nevada). This might be called the acid-leaching method.

The ore (1.3 to 2 per cent Cu) is dumped into tanks 88 feet square, 17 feet deep, made of reinforced concrete, with wooden bottoms, and leached 8 days on the countercurrent principle. The copper sulfate liquor with 2.985 per cent Cu is passed into the electrolytic deposition cells, with (impassive) lead anodes, and copper sheet cathodes, on which latter the liquor deposits a part of its copper; the outgoing liquor with 2.513 per cent Cu and a gain in sulfuric acid is strengthened by further leaching and reaches the cells again; this is continued until the impurities have accumulated so much that the liquor must be discarded. The remaining copper is then precipitated by scrap iron.[7]

[6] Chapter 48.

[7] "First year of leaching by the New Cornelia Copper Co.," Henry A. Tobelmann and James A. Potter, *Am. Inst. Mining Eng. Bull.*, No. 146, 449 (1919). *Compare* also the article by William E. Greenawalt, "The Greenawalt electrolytic copper extraction process," *Am. Inst. Mining Met. Eng.*, 70, 529 (1924).

In the early days of copper mining in Michigan, the tailings, still containing an appreciable percentage of copper, were washed into the lake from the stamp mills; now that the mine shafts must be deeper than formerly, operation costs have risen and it has become profitable to work over the discard of former days. This is done in part by concentrating by means of classifiers and shaking tables, the remainder by leaching with an ammonium carbonate solution.[8] Acid leaching would not do, for the gangue is mainly calcite, which would consume the acid.

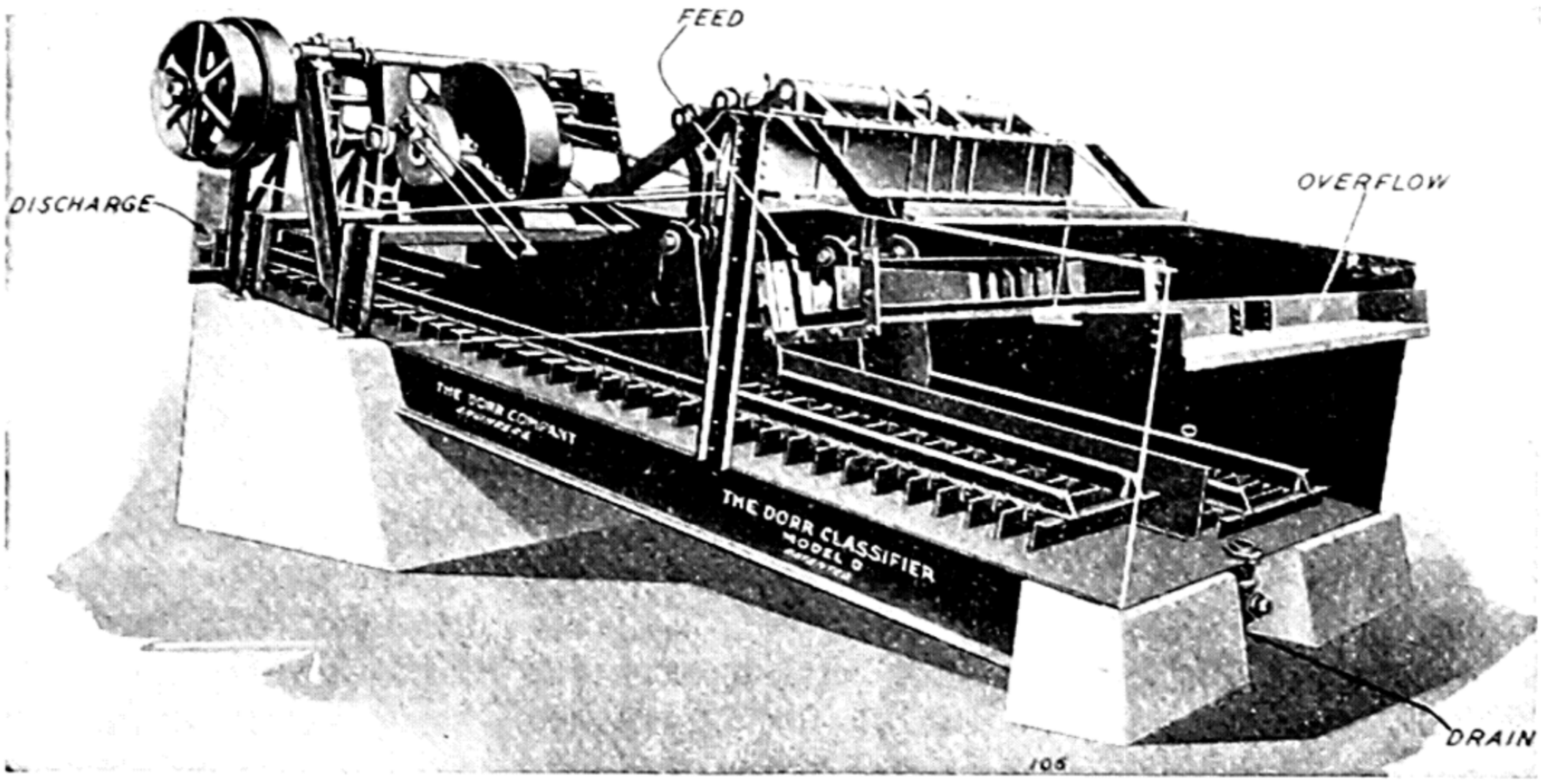


FIGURE 344.—The Dorr classifier, with inclined trough, rakes which sweep up, then are lifted out by a cam for the return stroke. (Courtesy of the Dorr Co., Inc., New York.)

The old discard from the stamp mills, with 0.8 per cent Cu, is brought up from the lake bottom by sucker dredges, screened twice, and classified. The Dorr classifier, for example, is of the drag type. It consists of an inclined trough in which scraper blades move in the sand toward the upper end, returning to their first position while raised and outside the sand. A stream of water carries down the lighter particles which the blades dislodge, while the heavier particles are pushed up along the floor and are finally discharged at the upper end. This upper discharge called the "sands" and richer in metal now, is ground in a Hardinge[9] mill, concentrated, and the concentrated portion sent to the smelting furnace. The weak tailings after suitable classification and concentration reach the leaching tanks. These are steel tanks 54 feet in diameter, 12 feet high, provided with covers; the contents of such a tank are percolated with the ammonium carbonate solution for 72 hours. At the end, the copper solution is evaporated in tank-like stills, the ammonia recovered and used again,

[8] "Ammonia leaching of Calumet and Hecla tailings," C. H. Benedict and H. C. Kenny, *Am. Inst. Mining Met. Eng.*, 70, 595 (1924).
[9] Chapter 44.

while the copper is left behind in the form of oxide. The residue in the leaching tank is washed and returned to the lake.

The chemical action is as follows: Cupric ammonium carbonate with excess ammonium carbonate dissolves native copper in the old discard, to form cuprous ammonium carbonate. This latter solution is the one which is distilled. The solution of cupric ammonium carbonate required for the extracting solution is obtained by treating a portion of the cuprous ammonium carbonate solution with air.

Still another wet extraction method which deserves brief mention is the one practiced at Rio Tinto, in Spain. The iron pyrite mined there contains 3 per cent copper. It is extracted by oxidation of the copper glance, Cu_2S, and washing out the copper sulfate formed. The ore is piled in heaps 30 feet high containing 100,000 tons; draft pipes are built into the heap, and the top has grooves and basins for the distribution of water. The wash water is passed over pig iron, which precipitates the copper metal. One-half the copper in the ore is washed out in 3 months, 80 per cent of the other half in 2 years. The ore is called washed when the copper content has been reduced to 0.3 per cent. The oxidation of the copper sulfide is due to the action of air and of ferric sulfate.

Electrolytic Refining of the Crude or Blister Copper. The crude copper with 98 per cent Cu is made into pure copper by electrolysis in a solution of copper sulfate kept slightly acid by sulfuric acid additions. For many years, the native lake copper was quoted one-eighth cent higher than electrolytic; lake copper is very pure, and very small amounts of impurities affect the properties of the metal to a considerable extent; it is now generally recognized that electrolytic copper made from sulfide and other ores is the equal of native or lake copper. The blister copper is cast into anodes, flat sheets 3 feet long by $3\frac{1}{2}$ feet wide, and three-quarters of an inch thick; these are suspended at a distance of 2 inches from the cathode, a copper sheet of similar dimensions except that it is as thin as paper (0.01 inch). The direct current passes through the solution; the anode decreases in thickness, while the cathode gains. During the transfer of the metal, the impurities are removed in various ways. The noble metals, silver and gold, drop off as the copper disintegrates, and deposit as the anode mud, worked up later into the precious metals. Nickel, cobalt, iron and zinc dissolve and remain in the solution; lead and bismuth form a sulfate mud; arsenic forms an insoluble arsenate with copper, and also drops into the mud. Every time an anode is replaced, the muddy liquid is pumped out.

By maintaining the proper voltage, none of the impurities plate out with the copper, hence its purity. The current density is 15 amperes per square foot of surface, the voltage 0.3 to 0.35 per plate, and the temperature 130° F. The electrolyte is circulated and periodically changed in order to remove the gradually accumulating soluble non-copper salts.

The cathode plates are remelted and cast into ingots, more convenient to handle; at the same time, the density is raised and the leaf-like structure removed.

Of the domestic production of primary copper, 82 per cent is electrolytically refined, 3.8 is Lake copper, 14 per cent is casting copper. Foreign primary copper is 100 per cent electrolytic.

Lead

The important lead ore is galena, the sulfide, PbS, a black ore which is sometimes found well crystallized; its purity varies in the different deposits. Lead is also obtained from a mixed lead and zinc sulfide, and this in addition may contain silver. The production for the different countries is given in Table 156.

Table 156.—*World production of lead (in metric tons).**

	1943	1946
United States	425,903	306,717
Mexico	212,452	137,742
Canada	203,051	150,360
Australia	192,322	153,556
U.S.S.R.	110,000	—
Peru	43,171	36,478
Spain	36,760	32,346
Japan	32,511	—
Argentina	23,800	16,190
Korea (Chosen)	18,467	—
France	12,428	34,680
Total world	1,575,000	1,166,000

* Minerals Yearbook.

In the production of lead, the United States leads; for the several States, the figures are as listed in Table 157.

Table 157.—*Mine production of recoverable lead, by districts (U. S.) (in short tons).**

Southeastern Missouri region	179,012	135,796
Coeur d'Alene region, Idaho	89,813	56,548
Tri-State (Joplin region)	34,722	23,363
Bingham, West Mountain, Utah	35,437	12,343
Warren (Bisbee) Arizona	712	10,889
Park City region, Utah	16,022	8,373
Total	453,313	335,475

* Minerals Yearbook.

Two-thirds of the Missouri production of lead is from the southeastern portion of the State, where galena is found; the other third is from the southwestern part of the State, an area rich in zinc blende and lead-zinc sulfides; the main product in this area is zinc. The southwestern district is described in more detail under zinc, in the next division. Near Leadville, Colorado, the ores mined are mainly lead-zinc sulfides, carrying silver.

The method of extraction for galena ores includes a crushing and screening followed by classifying in a Dorr classifier or a similar device. The classifier delivers at one end the "sands," at the other, the "slimes." The sands are concentrated further on shaking tables, which yield con-

centrated ore, ready for smelting, and tailings which are treated further after pulverizing in a ball mill. The concentrated ore may be 60 to 70 per cent Pb, from an original ore 6 to 8 per cent Pb.

The slimes are thickened in a Dorr thickener and filtered, yielding a cake containing 60 per cent Pb.

The concentrated ore is smelted in a square blast furnace not over 10 feet high, or on a hearth; an improved form of the latter is the Newnman hearth, much favored in Missouri.

A simpler hearth for lead smelting is a shallow cast-iron box in which ore, fuel, and flux are placed, while the blast is applied from the rear, downward. The hearth is similar to an ordinary blacksmith's forge. The metal reaches the bottom and is siphoned off. Fresh ore and fuel are spread on constantly, and the mass is rabbled by hand. In the Newnman hearth, the rabbling is mechanical; its size is 8 feet in length, 20 inches wide and 8 inches deep, and its capacity is over three tons of lead produced in 8 hours.[10]

In the blast furnace, the ore mixed with the flux, which may be iron oxide and lime, and with coke as fuel, is fed in. Lead in the liquid form collects at the base and retains any silver or gold which the ore contained. The lime displaces the lead in any lead silicate which might have formed, while the iron oxide binds the sulfur which fails to burn off as sulfur dioxide, as iron sulfide. The lead and slag are tapped at different levels, very much as is done with pig iron in the iron blast furnace. The iron oxide used in the charge is generally cinders from iron pyrite from the sulfuric acid plants.

When silver is absent, the first product is freed from antimony, tin, copper, zinc, sulfur, and iron, present in small amounts, by melting the lead and maintaining it at red heat in a reverberatory furnace. The impurities as oxides (except zinc) mixed with lead oxide (litharge, PbO) form a skin on the surface which is removed from time to time; to facilitate the removal, some lime is added, which stiffens the oxides. The zinc oxide passes off in the fumes.

If silver is present in small amounts, it is removed by melting the lead in one of a series of pots and allowing it to cool slowly; the lead, free from silver or poorer in silver, separates as crystals which float at the surface, leaving the silver-containing lead, or richer lead, in the molten state. The crystals are ladled into the pot on the left, the melted lead into the pot on the right. The operation is repeated, until on the left lead free from silver is obtained, while on the right a lead rich in silver is collected. This process is known as the Pattinson process, which is used in Great Britain and on the Continent.

The silver-rich lead may be concentrated in another way, namely by adding melted zinc, which alloys with silver (gold at the very first, if any present) and forms a scum which contains the silver, leaving a melted lead poorer in silver. The separation of the silver is not complete, and must be repeated several times. The scum is distilled for zinc in graphite retorts, leaving lead and silver; this is treated for the recovery of the

[10] *Trans. Am. Inst. Mining Met. Eng.*, 54, 485 (1917).

silver as described in the next chapter under silver. The zinc process is called the Parkes process and is the standard process in the United States. There is a variety in the details of treatment in the various plants, designed to suit the particular ore treated.

The lead free from silver may now be purified in a reverberatory furnace, as described three paragraphs back.

A somewhat different procedure is the Harris process, in which crude melted lead is agitated with molten caustic (NaOH), which removes all the undesirable metals, including arsenic, but does not affect the lead nor the silver. The purified lead is then desilverized.

A portion of the lead production, perhaps one-quarter of the total, is consumed in making white lead and other pigments.[11]

In 1944, 83,067 tons of lead were consumed in the manufacture of tetraethyl lead to be added to gasoline, mainly for military aircraft; from this high figure, the amount dropped to 47,965 tons in 1946.

Quality of Ores. When copper is present in an ore forming part of mixture smelted in the lead blast furnace, the aim is to recover it in the form of matte (copper sulfide), which forms a middle layer, with the slag over it, the melted lead under. The matte forms only if enough sulfur is present.

Zinc is not recovered in the copper nor in the lead-smelting operations, but passes to the slag in part, and to the fumes. Over 10 per cent of zinc in the slag makes it viscous, decreasing furnace capacity; in the fumes, the zinc increases losses by volatilization. There is therefore a penalty of 30 to 50 cents for each per cent zinc above 1 per cent per ton. This heavy penalty has stimulated efforts to separate zinc blende from lead or copper before selling the ores to the smelter.[12] There is a bonus on iron because it fluxes out the silica without requiring the addition of purchased limestone. There is a penalty (light) for silica above a certain percentage.

Zinc

The zinc ores of industrial importance are the sulfide, ZnS, called zinc blende, and the carbonate, called calamine. The sulfide is white when pure, but the ore is generally brown or black from admixed iron or lead. The mixed sulfides of lead and zinc are also used, for both their metals. Zinc blende is more important than calamine. To these may be added franklinite, a double oxide of iron and zinc, and willemite, a zinc silicate, both found at Franklin, New Jersey, and actively mined.

The output of spelter (zinc metal) in the several countries[13] is given in Table 158; in a general way, the figures also indicate the production of zinc ore in the countries named. It will be observed that the United States retains the lead in zinc production which it has in lead and copper.

[11] Chapter 31.

[12] *Bur. Mines Tech. Paper* No. 83, Ch. H. Fulton (1915).

[13] In Belgium, the main mine is the Moresnet, on the German border; it has yielded calamine, blande, and galena for many generations, and has been in continuous operation since the 15th Century (Vieille Montagne Company). Of late, its output must be supplemented by imported ores.

TABLE 158.—*World smelter production of zinc by countries where smelted, in metric tons.**

	1943	1946
United States	854,844	660,665
Germany	312,000	28,429
Canada	187,342	168,431
Australia	76,972	78,540
United Kingdom	70,345	66,405
Japan	60,948	—
Mexico	54,449	41,982
Belgium	27,770	86,224
Total world	1,830,500	1,406,500

* Minerals Yearbook.

Within the United States the order is also quite different than it was in 1943; In Table 159, the mine production of zinc ores, calculated to zinc metal, is stated.

The mine production does not quite agree with the spelter production because there is a loss in smelting, and because ores are stored and worked up perhaps a year later. The tri-state district is placed together because, although part of three States, it is geologically a single deposit. Its area is only some 10 or 15 miles square; it lies in three contiguous

TABLE 159.—*Mine production of recoverable zinc, by districts (U. S.) in short tons.**

	1943	1946
Tri-State, Joplin region, Kansas, Missouri, Oklahoma	200,514	139,038
Coeur d'Alene region, Idaho	79,634	67,429
New Jersey	92,864	64,451
St. Lawrence County, N. Y.	46,000	32,515
Central New Mexico	52,215	32,279
Eastern Tennessee	41,766	24,614
Warren (Bisbee), Arizona	1,020	22,374
Upper Mississippi Valley	15,539	18,344
Total	744,196	574,833

counties, Ottawa (Oklahoma), Cherokee (Kansas), and Jasper (Missouri), of which Ottawa County is at the present time the best producer. Joplin lies in the district, in Jasper County. As the table shows, this district is the prime producer in the United States. The ore is mainly zinc blende.

After crushing, the ore is concentrated in jigs, shaking tables,[14] and by oil flotation; still another device sometimes used for zinc ores is the electrostatic separator.[14a] The concentrated ore is roasted in rotary shelf burners, which are the prototype of the rotary burner used for iron pyrite burning[15]; the sulfide is thus transformed into the oxide. The reduction of the oxide to the metal is performed in rather small, horizontal fireclay retorts, banked over each other, and set in a furnace receiving preheated gas and air; in this way, a high heat is applied to the retorts, and the metal

[14] Chapter 50.
[14a] Sutton, Steele, and Steele, Manufacturing Engineers, Dallas, Texas.
[15] Chapter 1.

formed within them is distilled into the fireclay receiver placed at the mouth of the retort. The volume of the retort is 1.5 to 1.9 cubic feet, which is filled with finely divided oxide mixed with 25 per cent non-caking coal. The receiver is capped by a third piece, the condenser, in which the first vapors of the metal condense as a dust (zinc dust); receiver and condenser have an opening through which the carbon monoxide formed passes out; it burns at the outlet from the condenser. The charge for a retort is 40 to 50 pounds of oxide. The metal for the main part collects as a liquid in the receiver, and is removed by a ladle. The number of horizontal retorts reported at active horizontal retort primary plants in 1946 was 73,240. This number of retorts was distributed among 20 plants, perhaps 60 to a furnace for the largest furnaces (estimate).

There are also in active operation vertical retorts, which may be heated electrically or by flame, and which have continuous feed, distillation and discharge. Of a total of 75 vertical retorts in four plants, 9 retorts are electrothermic units.

In the case of ores containing both zinc and lead, with the zinc above 10 per cent, the practice is to work the ore in the retorts for zinc, as described above. The residue is then handled as a lead ore would be. With the zinc below 10 per cent, the ore is worked for lead, and the zinc passes out as oxide in the fumes.

Electrolytic Zinc. Just after the war of 1914-18, electrolytic zinc was a curiosity; since then the demand has steadily increased. Of the United States production (1946) of primary metal, 39 per cent is electrolytic zinc, 61 per cent is distilled zinc. Electrolytic zinc has high purity, 99.999 per cent, which gives it superior properties, particularly corrosion-resisting qualities. Its high purity is primarily the result of the necessity of having the deposition bath absolutely pure, if any zinc is to be deposited at all.

The roasted ore is dissolved in the spent acid from the cells, iron added to remove arsenic and antimony, manganeses dioxide (if not present in the ore) to oxidize the iron, zinc oxide to precipitate the iron, and zinc metal to remove copper, cobalt, and nickel. The resulting pure solution is then electrolyzed.

Indium Extraction. Indium occurs in many zinc ores, and may be isolated by using the following sequence of operations: [15a] the ore concentrate, mainly sulfides, is roasted (at 400 to 600° C. (752 to 1112° F.)) to produce a calcine, mainly oxides. The calcine is leached in a series of Pachuca tanks with sulfuric acid. The solution carries Zn, Fe, Au, Ag, As, Sb, and substantially all the indium. The acid solution receives calcium carbonate in the last tank, which causes the separation of In, some Fe, Au, Ag, Cu. This precipitate is now treated in other Pachucas with acids, with air agitation. The metals redissolve. The solution is treated with zinc metal, so that In, Au, Ag, Cu separate in the metallic form. These solids are treated next with 25 per cent sulfuric acid for 1½ hour, and the solution so obtained receives hydrogen sulfide, which throws out Au, Ag, and Cu as sulfide, but not the indium. The slurry is filter pressed, the filtrate blown

[15a] U. S. Patent 1,847,622; *see* also 1,839,800.

free of hydrogen sulfide, and sent to the electrolytic tanks, where the indium is plated out, practically pure.

Moistening the ore concentrate with sulfuric acid, and roasting this wet concentrate at 1100 to 1250° F. (593 to 677° C.) leads to increased yields of indium.[15b, 15c] (*See* under Silver in Chapter 50.)

Another method provides for the recovery of indium (and gallium) from the lead-containing retort residues in the zinc distillation process.[15d]

Indium improves corrosion resistance, and permits bearing surfaces to retain a more complete film of oil; it is used in plating special alloys and in making low-melting alloys.* Indium metal itself is soft, almost like putty. The production dropped from 57,434 troy ounces in 1945 to 9,667 ounces in 1946.

Tin

Tin until 1939 was smelted mainly in England, Holland, in the Netherland Indies (Batavia), and in Malaya. In 1941, the Defense Plant Corporation ordered a smelter erected at Texas City, Texas, now known as the Longhorn smelter. It was constructed and is operated by the Tin Processing Corporation, a subsidiary of the N. V. Billiton Maatschappij of Batavia, and is owned by the Government. Its operation began in 1942. The 1946 domestic production of primary tin, 43,500 long tons, is essentially that of Longhorn, for which three quarters of the ore was Bolivian low grade ore (average 37 per cent Sn). There are no tin ores in the United States. Supplementing the smelter production, there were imported 15,520 long tons of tin metal. The world production of tin was 92,000 long tons in 1946, which may be contrasted to the peak production of 225,000 tons in the war year of 1941.

The main producing countries of tin minerals, mainly tinstone, the oxide, were, in 1946: Bolivia, 37,717 long tons; Belgian Congo, 14,095; Nigeria, 10,333; British Malaya, 8,432, just one tenth of its 1940 production; and the Netherland Indies 6,535 tons, about one-eighth of its 1941 production. The world production of tin minerals was 78,000 long tons (1946). With improving conditions, the former leaders will show better annual figures.

The metal is obtained by reducing the ore, which is generally the impure oxide, SnO_2, with coal on the hearth of a reverberatory furnace. The crude metal so obtained is refined by placing it, after solidification, in the furnace and heating gradually, so that the melting is slow; the first metal is the purest; this system is called liquation, and is used for some of the other metals also. A further refining is by melting the metal in a pot, and suspending in it poles of green wood; the gases formed agitate the metal, and the impurities oxidize, forming a scum which can be removed. Poling is used for other metals also.

The uses to which the metal was put in 1946 were as follows: tin plate 48 per cent of the virgin metal; solder, 25; brass and bronze, 9; babbitt metal, 8.

[15b] U. S. Patent 1,912,590.
[15c] Silver-indium alloys are presented in Chapter 50.
[15d] U. S. Patent 1,855,455; 1,886,825.
* See "Minor metals," Minerals Yearbook 1946.

Mercury

The chief ore used for the extraction of mercury is the sulfide, HgS, cinnabar, a red ore. The chief United States producer has been California (the New Idria mine in San Benito County).

Table 160.—*World production of mercury in flasks of 34.5 kilograms (76 pounds).**

	1941	1943	1946
Italy	94,160	60,000	49,314
Spain	86,473	47,756	41,000
United States	44,921	51,929	25,328
Mexico	23,137	28,321	11,661
Canada	7,057	22,240	none
Total	275,000	235,000	139,000

* Minerals Yearbook.

The production for mercury is usually given in terms of flasks (made of cast iron) of 76 pounds each. In the arts, mercury is used less than formerly. It is still used in countless ways of semi-scientific nature, but in amounts very small. A considerable use remains in dental fillings, and even this use will call for less new metal than formerly (at least in proportion) now that the mercury from the waste amalgam is recovered. Mercury is consumed for the manufacture of mercury fulminate, which has held its place for the explosives of war as well as peace explosives. It is this demand which has stimulated the production. Mercury as the working substance in boilers and turbines is presented in Chapter 12.

Cinnabar is roasted; the free metal and sulfur dioxide form. They pass together into a series of chambers where the velocity of the gas is reduced; the mercury deposits, while the sulfur dioxide passes out. The partly cooled gases may also be passed through small air-cooled glass condensers (aludels). The metal may be refined by distillation. Mercury alloys with many metals, to form "amalgams," but not with iron; the metal it attacks easiest is gold.

Nickel

Almost no nickel is mined in the United States. The world production of nickel in 1946 was 140,000 short tons, of which Canada produced 94,833. The second producing country is Cuba, with 11,241 metric tons of nickel (content of ore). New Caledonia produced 2,779 short tons of nickel (content of ore, which is about a fourth of its 1941 production).

The chief ore is pendlantite, a complex sulfide of iron, copper and nickel found in the Sudbury district, with a nickel content of 3 to 3.5 per cent. Monel metal is discussed in Chapter 45. The deposits in New Caledonia in the South Pacific, the main source of nickel until the Sudbury basin was discovered, consist of an oxidized ore of the garnierite type.

At Copper Cliff (Sudbury) the mixed sulfides are ground fine, classified, roasted in Herreshoff burners to remove some of the sulfur, smelted in reverberatory furnaces and blown in Bessemers with addition of silica-bearing fluxes to remove most of the iron as a slag. The still impure mixed copper and nickel sulfide is then treated by a special process (Orford) in

order to concentrate each. It is heated in a reverberatory furnace with sodium sulfate and some coal, so that sodium sulfide results. An essentially homogeneous melt results, which is run into medium-sized receptacles and allowed to cool slowly. There is formed at the bottom a hemispherical cake of nickel sulfide with still some copper sulfide, over it, a "tops" of copper sulfide with still some nickel sulfide, and throughout both, sodium sulfide. The bottoms are concentrated further by a second melting, and perhaps a third; similarly the tops. The separation is a physical process; the sodium sulfide serves as floating agent.

The bottoms with 74 per cent Ni and 1.5 per cent Cu are sent to Port Colborne, where they pass successively through a jaw crusher, a ball mill, a 10-mesh screen, to reach a rectangular lead lined tank with false bottom. In this tank, the ground material is leached with hot water to remove sodium sulfide, then, with sulfuric acid to remove most of the remaining iron. The nickel sulfide, now with 76 per cent Ni and 24 per cent S, is divided, and treated further in two ways. One is by roasting on a Dwight-Lloyd sintering machine; the resulting oxide is mixed with 20 per cent coal and heated in an open hearth furnace to give the liquid metal, 96 per cent pure (2 per cent Cu, 1 per cent Fe, S, Co), which is cast, when the furnace is tapped, into thick slabs weighing 490 lbs. These are purified by electrolysis.

The other way is by calcining in a one-hearth calcining oven, with rabbles which stir the ore and also move it at a slow rate toward the hot end, where an oil flame supplies an intense heat, in order to insure the removal of the last of the sulfur. The resulting nickel oxide goes in part to the Mond reducer, a shelf tower with rabbles, where it is reduced to nickel. In part, this metal serves in the purification of the electrolyte liquor, by precipitating an equivalent amount of copper. The black oxide is sold to a considerable extent to potteries for decorating tableware.

The Mond reducer works at 400° F. (204° C.), is 35 feet high and is built of cast iron sections, each having a heating chamber, surmounted by two shelves, one with central, the other with circumferential discharge. A central vertical shaft carries the arms and rabbles. The oxide moves down, as water gas passes upward; from the top, the not quite exhausted water gas is led back, and is burned to furnish the heat (supplemented if needed) to the heating chambers.

For the purification, the anode is suspended in a solution of nickel sulfate, and the metal driven across to the nickel starting sheet (28″ × 36″), itself produced by depositing the nickel for 3 days, from the same bath, on aluminum, then stripping off the thin nickel sheet. The anode cycle is 41 days. The electrolytic tanks are concrete, 5′ 2″ deep, coated with gilsonite, with divisions accommodating 31 anodes and 30 starting sheets, each anode facing a starting sheet less than 2″ away. The voltage is $2\frac{1}{2}$ volts; the current density 12 amperes per square foot. As the nickel anode dissolves, copper and iron enter the electrolyte; they are prevented from plating out by the continuous removal of the electrolyte to a purification system and the continuous infeed of purified electrolyte into a canvas box enclosing the cathode so that an electrostatic head can be maintained which

prevents the foul solution from reaching the plate. The precious metals, on the other hand, remain as a mud on the last thickness of the anode; they are collected, treated as nickel anodes again, for concentration, this time with bags around the anode. The anode mud is then collected and sent to Acton, England, for the recovery of Pt, Pd, Rh, Ru; there is no gold nor silver.

The purification of the nickel sulfate electrolyte is by treatment in Pachuca [16] tanks with nickel powder to precipitate copper, a Dorr thickener to remove remaining solids; oxidizers, followed by addition of nickel carbonate, to precipitate iron, and make good the resulting drop in p_H (rise in acidity); the electrolyte is kept at a p_H of 5.2. The liquor is filter-pressed, and is then ready to be fed back to the plating tanks. The capacity of the plant is 420,000 lbs. of 99.95 per cent nickel per day.

In the Mond recovery process, in operation in England, nickel in the metallic form is volatilized by means of carbon monoxide at 100° C. (212° F.) forming the gaseous $Ni(CO)_4$. Heated to 180° C. (356° F.), nickel carbonyl decomposes, leaving the metal behind; the monoxide may be used over again. The deposition is done in small towers, and on nickel shot from previous runs, which are screened to remove the larger sizes. The smaller sizes receive the new deposits, and acquire a structure very much like that of an onion. Before passing through the volatilizing tower, the ore goes through the reducing tower, similar to the system at Port Colborne, just described. The same ore passes reducing tower and volatilizing tower several times.

Late in 1946, nickel was quoted at 35 cents a pound.

Nickel is used in chromium-nickel stainless steels (36,000,000 pounds); in nickel-chromium-molybdenum steels; for electroplating, for making nickel-silver alloys, and for minting the five-cent piece.

Chromium

While fuel-fired furnaces have in the past produced an iron alloy with a maximum of 3 per cent chromium, the electric furnace produces alloys of any chromium content, even 99 per cent chromium. The uses for chrome steels and the importance of chrome plating have been discussed (Chapters 45 and 48). Nichrome is a nickel-chrome alloy, with high resistance to the electric current. Stellite contains chromium, cobalt (75 per cent) and tungsten; it is used for high-speed cutting tools, for gears, valves, lathe centers, etc. It is non-magnetic.

The chief ore is chromite, $FeO \cdot Cr_2O_3$, with a content of 48 or 45 per cent Cr_2O_3 in the higher grades. The consumption of chromite in the United States in 1946 was 734,759 short tons, of which all but about 4,000 tons had to be imported. The chief producers of chromite are Union of So. Africa 188,928 metric tons; Cuba, 174,170; So. Rhodesia, 151,433; Philippines,

[16] A Pachuca tank is a tall tank 30 feet to 40 feet high, 14 feet in diameter, with a conical bottom, generally built of wood. A hollow column is set upright in the center of the tank. A stream of compressed air is fed in at the base of the column, driving the "pulp" or slurry upward, and causing it to descend in the wider part of the tank. The air circulation may be supplemented by a stirrer, or a pump, or both.

58,000; New Caledonia, 24,946. The production in India in 1945 was 31,105 metric tons. The price of the ore varies; African and Indian ore were priced from $39 to $41 per long ton (1946).

Beryllium is obtained from Beryl BeO, the greater part of which is imported from Brazil (906 tons, 1946). It is reduced to the metal or alloys in the electric furnace. Addition of beryllium (2 per cent) to copper alloys hardens and strengthens them.

Columbium

In the treatment of stainless steels by columbium addition, in order to preserve their corrosion resistance even when heated, to improve their suitability to welding, and to manufacture complex non-ferrous alloys used for rotor wheels and blades for jet-propelled airplanes, relatively large amounts of columbium are required.[17] The main source is columbite, a complex ore selected preferably low in tantalum, for example, a columbite $Cb_2O_5 \cdot xTa_2O_5$ in which the Cb to Ta ratio is 10:1. The ore from Nigeria, a by-product of tin operations, is such an ore, of which 2,411,695 pounds were imported into the United States in 1946, which was half of the 1945 imports. A preliminary selective reduction is followed by chloridizing, in order to combine with tin, whose chloride then passes out by volatilization. The residue is reduced in the presence of aluminum, or silicon, in an electric furnace, with the production of a ferrocolumbium containing 55 per cent Cb, suited for steel making. There are modifications which lead to different products. The production per annum is estimated at 500,000 pounds of columbium, all of it produced and consumed in the United States.

Tantalum is obtained from tantalite, produced by the Geomines company in the Belgian Congo. The imports were 263,097 pounds, with furthermore 98,072 pounds from Brazil.

Molybdenum is a metal of which the United States has an ample supply. The main producing mine is at Climax, Colorado. The production of molybdenite for the whole country in 1946 was 16,304,000 pounds, compared to 66,437,000 pounds shipped from the mines in 1942. The ore is concentrated by flotation to 90 per cent MoS_2. Molybdenum in high speed tools has been mentioned; it is prized as an alloying metal in many steels of the machine and tool grade.

Additional Properties and Uses of the Metals; Alloys

The main use of copper is for electric motor and generator construction and for transmission lines, as stated in the introduction; it is also used for roofs, flashings, gutters, and conductor pipes; a copper roof coats itself with a layer of green carbonate and oxide which prevents further action. Lead when freshly scratched has a bright surface, which, however, tarnishes within a few minutes; lead is soft, and as such is used in the chemical industries[18] and for covering electrical cables placed underground and undersea. Lead is hardened by adding 1 to 10 per cent antimony. Lead

[17] "Columbium, from a laboratory curiosity to a widely used commercial product," James H. Critchett, *Trans. Electrochem. Soc.*, 69, 63 (1936). See Chapter 48.

[18] Chapter 45.

and zinc for storage batteries and dry cells respectively have been mentioned. Both of these metals are made into pigments, and the interesting suggestion has been made, now that titanium pigments are available, that the lead be reserved for storage battery work, letting the titanium pigment replace white lead.[19] Lead wire and ribbon are used for electrical fuses. A considerable use for zinc is in galvanizing; in wartime, the supply must be conserved for the military needs. Tin plating is less important now than formerly. Lead (60 parts) and tin (40 parts) form the valuable and much-used solder. Nickel is electroplated on iron, or better, on iron previously plated with copper; the nickel coat has no luster until the article is buffed. A few statements concerning metals are condensed in Table 161.

TABLE 161.—*Properties of metals; prices in cents per pound, averages for the year.*

	1929	1932	1940	1946	Color	Specific Gravity	Melting Point °F.	Melting Point °C.	Electrical Conductivity
Copper	18.23	5.67	11.3	13.82	red	8.9	1891 or	1083	100
Lead	6.3	3.0	5.0	8.11	white	11.4	621 or	327	8
Zinc	6.49	2.88	6.3	8.81	white	7.2	786 or	419	27
Tin	45.19	39.12	49.82	54.58	white	7.3	450 or	232	12
Mercury ...	160.7	....	233	98.24	white	13.6	liquid		2

The prices for metals have fluctuated in recent years, advancing considerably. Copper in 1947 reached 21½ cents a pound, and two cents more in the next year; in June 1949, it was 17 cents. Lead was sold at 21½ cents a pound in 1948 and early 1949, but dropped to 12 cents in June 1949. Zinc in 1947 was 10½ cents a pound, 12 cents the next year, and reached 17½ cents in early 1949; it is now 9½ cents (June 1949). Tin by comparison did not rise markedly; it was quoted at $1.03 a pound in February 1949.

The alloys are very numerous, even of the type containing two metals only, for the proportions affect the properties materially; thus for brasses, which consist of copper and zinc, the color is affected, as well as strength, ductility, hardness, and malleability. Bronze is copper and tin, with perhaps a small amount of zinc. Bearing metal, such as Babbitt, contains tin, 89 per cent; antimony, 7 per cent; copper, 4 per cent (for Babbitt No. 1). There are other bearing metals in which copper is the main constituent, and still others which contain much lead; for example, Frary metal, 98 per cent Pb and 2 per cent Ba. Type metal must expand on cooling, so that the letters will be sharp; an example is the composition: lead, 80 per cent; antimony, 20 per cent. Fusible alloys for fire extinguishers (automatic) contain tin, lead, bismuth, and either cadmium or antimony. Brasses are yellow to red; bronzes are brown; all the other alloys given above are white.

OTHER PATENTS

U. S. Patent 2,062,869, conducting chemical and metallurgical operations in a rotary furnace; 1,849,293 and 1,965,251; improvement to the indium plating bath; Canadian Patent 315,060, process of recovering nickel, Robert P. Stanley, assigned to the International Nickel Company, 18 claims.

[19] Chapter 31.

Reading References

"The mineral industry during 1935," edited by G. A. Roush, New York, McGraw-Hill Book Co., 1936.

"Minerals Yearbook, 1946," published by the Bureau of Mines, Washington.

"The flotation process," H. A. Megraw, New York, McGraw-Hill Book Co., 1916.

"Copper from ore to metal," Hugh K. Picard, London, Sir Isaac Pitman & Sons, Ltd., 1928.

"Innovations in copper leaching employing ferric sulphate-sulphuric acid," Harmon E. Keyes, *Bur. Mines Bull.* No. 321 (1930).

"Lead, its occurrence, extraction, properties, and uses," J. A. Smythe, New York, Longmans, Green and Co., 1923.

"Tin, its mining, production, technology and application," Second Ed., C. L. Mantell, New York, Reinhold Pub. Corp., 1949.

"Tin and the tin industry," A. H. Mundey, London, Sir Isaac Pitman & Sons, 1925.

"Electroplating with chromium, copper and nickel," Benjamin Freeman and Frederick G. Hoppe, New York, Prentice Hall, Inc., 1930.

"The Tennesese copper basin," E. P. Poste, *Ind. Eng. Chem.*, 24, 690 (1932).

"Nickel in Canada, the rise of a great industry," A. H. Robinson, *Sands, Clays and Minerals*, 3, pt. 1, 11-20 (1936); with 1 map and 7 pictures. (Publisher: A. L. Curtis, P. O. Box 61, Chatteris, England.)

"Indium available in commercial quantities," William S. Murray, *Ind. Eng. Chem.*, 24, 686 (1932).

"Production of beryllium oxide," H. Lundin, *Tr. Amer. Inst. Chem. Eng.*, 41, 671 (1945).

"Recent progress in the metallurgy of malleable zirconium," W. J. Kroll, The Electrochemical Society, October, 1947.

For many centuries, gold has been a synonym for wealth; to find gold, man will undergo untold hardships and risk his life, as demonstrated in the gold rush to California in 1849, through the desert; and again in the Klondike gold rush of 1896. In numerous mining and smelting processes, on the other hand, it is a humdrum operation, without excitement; the gold is just a by-product of copper. Gold is a unique commodity in that its price does not fluctuate with supply and demand, but is fixed by law. The former figure of $20.6718 per fine ounce was changed through decrees and legislation between August 9, 1933, and January 31, 1934, to $35.00. In terms of gold, the dollar is cheaper.

Chapter 50

Gold, Silver, Platinum, Radium, Uranium, Thorium, and Cerium

The unit in which prices for metals are quoted varies; pig iron is quoted by the ton; copper by the pound; but the precious metals are so valuable that they are quoted by the ounce. Gold has a fixed price,[1] $35.00 a troy ounce (31.10 grams), the figure which superseded the previous one of $20.67, in 1934.

Silver formerly varied in a free market, but in 1939, its price was stabilized at 71.11 cents a troy ounce; a later act, in 1946, had the effect of raising the domestic primary silver price to 90½ cents. For comparison, the open market figure was 38.47 cents a troy ounce. The O.P.A. price for platinum, $35 a troy ounce, was suspended April 29, 1946; in September of the same year, a high of $93 a troy ounce was reached, but by the end of the year, the price was $56 an ounce. Palladium continued at its O.P.A. price, $24 an ounce, through the year. Osmium, iridium and rhodium are also precious metals; iridium fluctuated between its O.P.A. price of $165 an ounce, and $110 on the free market. In a general way, the price reflects the scarcity of the metal; the scarcer the metal, the higher the price. A high price also acts as a conservator, for at the higher price only applications are made in which the metal is indispensable; there is no waste in its use for other applications in which a substitute would serve equally well.

Radium belongs to the precious metals as far as price goes, but it is not prepared in the metallic form; it enters the market in the form of radium bromide, $RaBr_2$. It occurs in such small quantities and the extraction process is so long, that it is quoted in gram lots, in the neighborhood of $30,000 per gram. The total amount of radium in the world in the form of marketable salts is estimated at not much over one pound (1946).

Closely allied to radium is uranium, its parent substance. With the discovery that Uranium 235 was fissionable, when bombarded with neutrons, and that Uranium 238 could be transformed into plutonium, again by neutron attack, and that plutonium was also fissionable, with the transformation of part of its mass into its energy equivalent, uranium became a metal with international importance. Uranium is the source of plutonium for military

[1] Gold Reserve Act, January 31, 1934. For silver, the Act of Congress of July 6, 1939.

bombs, and a potential source of useful energy in the course of its nuclear transformations.

Thorium and cerium are "rare earth" metals; they enter the market as alloyed metals in pyrophoric (fire-producing) alloys, or as oxides, such as in Welsbach mantles. In addition, thorium, like uranium, is a potential nuclear fuel.

Gold and the platinum metals are found mainly in the free or metallic state (native metal); silver occurs partly native, partly as sulfide and other compounds. Native gold is rarely free from silver. In addition to deposits worked solely for their precious metals, there are many copper and lead ores which contain silver and gold, and these "values" are isolated in the process of refining.

The precious metal scrap is saved with great care and brings high prices; it is reworked into pure metals and useful shapes; as a result more finished metal is refined than the amount of ore mined would indicate.

Gold

Gold is produced in many parts of the world, as partly indicated in the table below.

TABLE 162.—*World production of gold by countries, in fine ounces (1946).**

Union of So. Africa	11,917,914	Mexico	420,500
U.S.S.R.	6,000,000	Belgian Congo	331,304
Canada	2,807,643	Chile	230,521
United States	1,462,354	Brazil	200,000
Australia	824,480	Nicaragua	181,615
Gold Coast	587,000	Peru	158,378
Southern Rhodesia	544,596	India	131,680
Colombia	437,176	New Zealand	119,271
		Total	27,777,000

* Minerals Yearbook.

Within the United States and territories, the distribution of production is shown in the table below.

TABLE 163.—*Mine production of gold in continental United States, in fine ounces (1946).*

California	349,970	Colorado	129,604
South Dakota	307,647	Nevada	89,924
Alaska	192,303	Montana	62,350
Utah	152,228	Washington	49,911

Gold occurs native in two kinds of deposits: hard ores which must be crushed to free the granules of gold, and aluvial gravel which may be dredged. The hard ores are generally "free-milling ores," that is, on crushing them under the hammers (stamps), the gold is freed enough to be extracted by amalgamation or by cyanide solution. The hard ores include the auriferous iron pyrite, in which the gold is in the free state, and may be extracted by the cyanide solutions, without preliminary roasting, but not by mercury. In combined form the chief ore is the telluride. The second form in which gold-bearing material occurs is as alluvial deposits, chiefly

gravels found in the beds of certain present rivers and of rivers of prehistoric times. Within the United States, about as much gold is obtained from lodes (that is, hard rocks) as from gravel. The gravel deposits are called placers, and may be mined for less money than the hard rocks, for the gravel does not require crushing.

Gold nuggets of various sizes have been found in several parts of the world, the largest containing 2284 ounces of gold (Victoria field, Australia), and give the impression that gold-bearing material is rich, but the opposite is true. Nuggets are exceptional, and rich veins of gold are rare; the amount of gold in the ores is generally extremely low. Hard rocks with 1 part of gold to 70,000 parts of worthless gangue are common, while ores with 1 part in 300,000 [2] may still be worked at a profit. For placer deposits, the amount of gold may be still lower and still permit profitable operation.

Gold-bearing Quartz and Other Hard Rocks. Gold-bearing rocks are usually discovered by an outcrop, which soon leads into the ground so that shafts must be constructed and the ore lifted to the surface. It is crushed in gyratory [3] and jaw crushers,[3] or stamps, of which the latter are the older practice. A stamp battery consists of 5 hammers (stamps) with long stems; they are lifted by a cam, and drop by gravity onto the ore resting on a steel die at the bottom of a cast-iron crucible which accommodates 5 dies. Water enters from one side and leaves carrying the crushed rock on the other. The slurry may be worked for its gold in several ways; it is allowed to flow over slightly inclined amalgamated copper plates, which retain the gold, allowing the gangue, but also the auriferous pyrite, to pass. The discharge from the plates is then extracted with cyanide solution. Or, mercury may be added to the stamp crucible (direct amalgamation). The amalgam from the plates (scraped off) or from the stamps is pressed in soft leather or flannel bags to remove the liquid mercury, and the remaining amalgam is retorted. The product from gyratory and jaw crushers is treated similarly. Not infrequently, the crushed material is first concentrated on a shaking, inclined table over which water flows, carrying off the lighter gangue; the concentrates only are passed over the amalgamated plates.

Cyanide Process. The tailings from the amalgamated plates still contain some gold, which may be recovered by treating them with a cold sodium (or potassium) cyanide solution in the presence of air. It is becoming the custom to dispense with the amalgam method of recovery and treat the crushed ore directly with the cyanide solution. The ore is first reduced to fine powder in a ball mill, and the product is then agitated, cold, in a series of tanks, with a dilute cyanide solution:

$$4Au+8KCN+O_2+2H_2O \rightarrow 4KAu(CN)_2+4KOH.$$

The cyanide method has among other advantages this one, mentioned before, that gold accompanied by pyrite may be extracted without roasting after fine grinding.

[2] The South Dakota mines at Lead and Deadwood recover gold worth $3.50 per ton of rock; the Dome mine at Porcupine (Ontario) recovers gold worth $7.80 per ton (based on $20.67 an ounce).

[3] Chapter 44.

The cyanide slurry is filter-pressed; the filtrate contains the gold. In order to isolate it, metallic zinc in the form of shavings is added; the gold powder with excess zinc is treated with sulfuric acid, which removes the zinc and leaves the gold. The latter is then melted with fluxes in a furnace and refined in any one of various ways. The precipitating reaction may be represented as follows:

$$2KAu(CN)_2+2Zn+2H_2O \rightarrow 2Zn(CN)_2+2Au+H_2+2KOH.$$

At some mines, the cyanide solution is passed into a pebble mill of the continuous type (Hardinge [4]) so that dissolving and pulverizing go on at the same time.

The cyanide solution leaving the zinc-gold is brought up to the standard strength, and is used over again.

Gold Telluride. Tellurides of gold are widely distributed, occurring for example at Cripple Creek, Colorado, in Calaveras County, California, and in western Australia. Calaverite is a bronze-yellow ore, $AuTe_2$, with a small amount of silver; 40 per cent Au, 56 per cent Te, 3.5 per cent and less Ag. Silver telluride with some gold (7 per cent or less) also occur. It must be roasted in a furnace in order to remove the tellurium as dioxide, before treating with cyanide.

Placer Mining. Placer mining furnishes about three-fourths of the world's gold; placers are the source of most of the gold in South Africa, Russia, the Klondike, and of part of the gold mined in California. The gold-bearing gravels at the surface of the earth are the result of the weathering and erosion of gold originally deposited in hard rock as lodes. It is reasonable therefore to look for a lode near-by when a gold-bearing gravel has been located; in many cases, the lode has been discovered. The large-scale method of operation is by dredging, washing the gravel on the boat, discharging the waste stones, and concentrating the gold from the sand on shaking tables. The dredge brings up the gravel by means of steel buckets on an endless chain; it is dumped into a trommel and rotated there while water is played on it; the sand passes through the perforations in the trommel and drops onto the shaking tables (also called classifiers) and concentrated there. The concentrates are carried to the extraction plant. Care is taken to dump the waste in one direction while the dredge moves forward in the other, so that no gravel will be reworked. One or two men operate the dredge.

Dredging is done not only on rivers which have a flow of water, but also in dry territory, provided water may be sent in by pipes from a river or lake not too far distant. A pit is dug, large enough to accommodate the dredge, and enough water pumped in to float it; operations then proceed as they would in a river.

Dredging is an extension of the hand operation called panning, still employed by prospectors and by individual operators without other equipment. The pan is a circular dish with a small pocket in the bottom; it is filled with gravel, and held under a gentle stream of water; on rotating it,

[4] Chapter 44.

the lighter parts are gradually floated off, and the gold particles are found in the pocket.

Hydraulic Mining. Another extension of panning is hydraulic mining, in which powerful streams of water discharged through nozzles as large as 11 inches in diameter are played in a solid column against the side of a hill whose gravel is gold-bearing. The gravel is floated along gullies to a sluiceway, an inclined plank floor with cross-pieces, against which the gold particles lodge. Once a week, or more often, the water is turned off and a "clean-up" performed; the cross-pieces are removed and the gold collected. Mercury may be added to the sluice box; it will lodge against the "riffles" also and retain the gold.

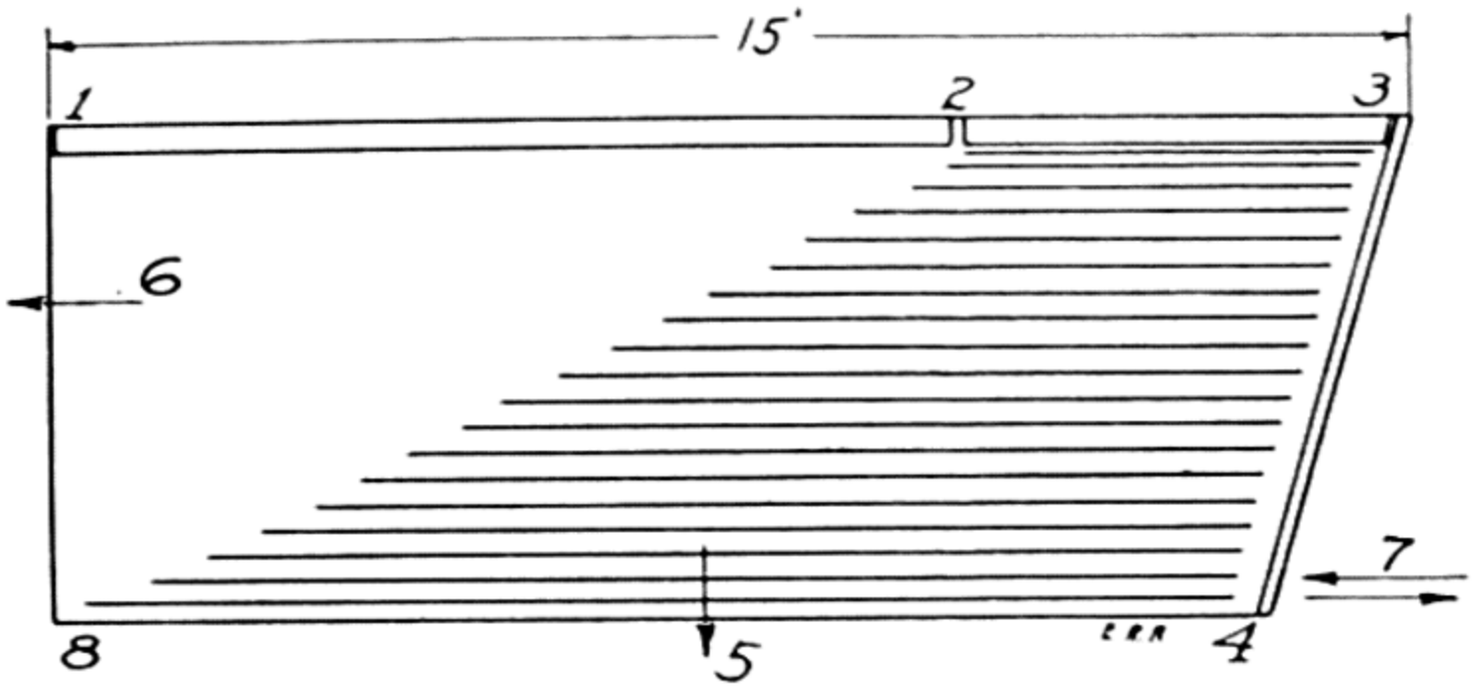


FIGURE 345.—Principle of a shaking table (Wilfley). Water enters from trough 1-2; slurry from 2-3; the table moves as shown by 7; 1-8 is several inches higher than 3-4, so that the concentrates move uphill and are discharged at 6; the gangue goes off at 5. The table is covered with linoleum, on which the riffles are tacked as shown. Moving mechanism not drawn.

Gold is rarely free from silver; placer gold is generally purer than lode gold.

Gold may also be removed from crushed rock or gravel by chlorination.

Purification of Gold. The native metal or metal recovered from scrap may be purified from base metals such as lead by the furnace process called cupellation and described under silver.

In order to remove any silver in the gold, either a sulfuric or nitric acid treatment is performed, or an electrolytic method, that of Moebius, is employed. In the acid method, the silver is dissolved and leaves the gold behind, but the protective action of the gold is so great that unless the silver present amounts to 80 per cent, the acid has no effect. Gold which contains less silver must first be melted with an extra amount before the separation from the silver, called the "parting," is effected.

The electrolytic method is the one usually employed in the United States. The anodes are doré silver, that is, gold-bearing silver; the cathode is a movable silver belt with a light coating of oil. The belt moves in a trough of redwood coated with an acid-resisting paint. The bath is silver nitrate, kept slightly acid with nitric acid. The belt moves under the cathodes and is brushed off automatically at the turn, delivering silver powder. Each

anode is hung in a fabric basket in which the gold slime deposits. The slimes are collected at intervals, washed with sulfuric acid, and melted for gold metal.

Properties and Uses of Gold. The pure metal may be hammered so thin that 250,000 sheets are required to make up 1 inch in thickness; the sheets are used for lettering book bindings. For coinage, gold is alloyed with copper, which hardens it; the pure metal is too soft for coinage purposes. The United States coinage is 900 fine[5] (900 parts gold and 100 parts copper). For jewelry, alloys with various proportions of gold are used, expressed in terms of carats; pure gold is 24 carat, 18 carat gold is 75 per cent gold. In dental work, gold is of great value, for it is unattacked by saliva or foods.

Gold is permanent in the air; it is unattacked by acids (except aqua regia and selenic acid); its characteristic yellow color is redder in copper alloys, greener in silver alloys. White gold is the palladium alloy.

Silver

Silver is found alloyed with gold, and to a minor degree, as metallic silver enclosed in silver ores; the more general occurrence is in the form of compounds, and of these the sulfide of silver, argentite, is the principal ore. As stated under gold, much silver is recovered from copper and lead ore, during the refining process. It is interesting to note that in several localities in which gold, silver, and copper have been mined, the gold is above the silver, and the silver above the copper, so that a mine started as a gold mine became a silver mine and later a copper mine as the depth of the shaft increased (Old Dominion Copper Company, Arizona). As with gold, much of the refined silver has its origin in silver scrap. The countries which produce the bulk of the new silver are indicated in Table 164.

Table 164.—*World production of silver, in fine ounces (1946).**

Mexico	43,263,132	Belgian Congo	5,047,666
United States	21,103,269	Honduras	2,682,910
Canada	12,676,928	Union of So. Africa	1,203,978
Peru	12,334,761	Japan	1,068,665
Australia	9,073,481	Spain	698,636
Bolivia	6,106,165	Chile	532,738
		World	129,000,000

* Minerals Yearbook. The production for Germany, Argentina, Sweden, Burma and Czechoslovakia large producers in earlier years (in proper order), is unreported.

Within the United States, the producing states rank as follows.

Table 165.—*Production of silver by States in the United States —fine ounces (1946).**

Idaho	6,218,895	Colorado	2,040,874
Utah	3,530,855	Nevada	1,339,421
Arizona	2,991,406	California	1,195,765
Montana	2,747,700	Total U. S.	21,103,269

* Minerals Yearbook.

[5] No longer binding by law; since April, 1933, the United States "has been off the gold standard," that is, the gold coin may be minted as low as 450 fine, at the discretion of the President.

In Guanajuato, the ore is of the free-milling type, with the metal in the native state; this district is losing in importance, while a new Mexican center, Parral, in Chihuahua, is gaining.

For the sulfide ore, argentite, the process consists of a roasting on the hearth of a reverberatory furnace, followed by addition of charcoal and further heating to reduce the oxide to the free metal, which is run off in the molten state.

If the ore is lead-bearing, as it often is, more lead may be added until a free-flowing (easily melted) metal is obtained from the first ore treatment, and this lead alloy is put through the process of cupellation which removes the lead in the form of the oxide, PbO, litharge, leaving the silver metal on the hearth.

The cupel might be described as an open-hearth furnace with the hearth of special construction; it is made by ramming bone ash into an iron form; the bone ash is moistened with a potassium carbonate solution. In the center a shallow depression is scooped out. After drying, the cupel bottom is ready for use. Its function aside from furnishing a refractory base of non-contaminating material is to absorb a portion of the fused litharge, litharge solution of base metals, and liquid slags formed by the addition of fluxes. The greater part of the litharge is run off through a gutter and collected; if made from a rich alloy, it may retain some silver and must then be reduced again in the reverberatory furnace, and cupelled again; if made from a weak alloy, it enters the market, and is used, for instance, for making the brilliant lead-potash glass for tableware. A lead alloy containing 500 ounces to the ton is considered a weak alloy; one containing 4000 ounces to the ton a rich one.

The process requires a blast of air directed onto the metals on the hearth, while at red heat. The end of the operation is reached when the last film of oxide is removed; the silver flashes out brightly, reflecting the arch of the furnace as a mirror would. The purity of the silver is 99.8 per cent, or 998 fine.

The cupel is used not only for silver but also for other precious metals; a silver-gold alloy is usually the result of cupellation. Bone-ash crucibles may be used as well as a hearth of bone ash.

Silver is prized for its beautiful color; its surface takes a high polish. Its uses depend in part upon its superior color and its stability in the air (jewelry, tableware). Silver coins usually contain 5 to 10 per cent copper.

An important use of silver is in photography,[6] in the form of silver bromide and chloride, sensitive to light; another commercial use of silver salts (the nitrate) is in making mirrors.

Indium. It was discovered that the addition of indium to silver renders such silver, whether solid silver or plated ware, tarnish-proof.[7] The indium may be incorporated in the silver by hanging two cathodes, one an indium rod, one a silver rod, in the plating bath, with the two double salts of potassium cyanide and indium and silver, dissolved in the plating bath; the object to be plated forms the cathode. With a density of .07 ampere per

[6] Chapter 37.

[7] Canadian Patent 338,197 and U. S. Patents 1,959,668; 1,847,941.

square inch, a deposit of 4 to 5 per cent indium is formed. By raising the current density to .1, a deposit with 11 per cent indium is formed. By varying the current density, the proportion of indium may be varied at will. A second method is to deposit alternate layers of silver and indium, and then to heat in an oven in order to allow the metals to diffuse. A bluish color which the indium imparts to silver is counteracted by a further improvement, namely, by depositing a silver-gold alloy [8] instead of silver, and alternating with indium. For example, 12½ per cent gold, 87½ per cent silver, alternating with indium, heating first to 110° C. (230° F.) for 8 hours, then to 165° C. (329° F.) for 18 hours. The yellow of the gold neutralizes the blue of the indium. The electrodeposition of indium is facilitated by the addition to the plating bath of an organic compound of an acid nature which has the effect of retaining the indium salt in solution, while without it, it tends to separate from the bath [9]; such a compound is glycine. The current density recommended in one example for the glycine-containing bath is .035 ampere per square inch.[10]

Indium plated on copper also produces a tarnish-proof surface.[11]

Platinum

Platinum is a white metal, more resistant to chemical agents than silver but not more beautiful in color. It is much heavier than silver (21.5 against 10.5). The production of platinum is usually less than that of gold. Formerly platinum was considered of no value [12]; with the development of chemical analysis, it was found that platinum vessels resisted heat and the action of most chemical reagents except aqua regia which dissolves it slowly, and some others.[13] For many years, sulfuric acid made in the lead chambers was concentrated in platinum pans; at the present time, it functions in a new way in the manufacture of the same acid, namely, as a catalyst.[14] Platinum is used extensively in jewelry. Among the many other services which this metal renders, its use in pyrometers must not be overlooked.

Platinum occurs nearly altogether as a native metal, alloyed with palladium, iridium, in alluvial deposits chiefly.[15] The principal regions of production are shown in Table 166.

In the United States the small amount of primary platinum in former years was a by-product of California placer gold; the increased production is due to workings on Squirrel Creek, Goodnews Bay, Alaska, started in

[8] U. S. Patent 1,934,730.
[9] U. S. Patent 1,935,630.
[10] For the source and extraction of indium, see Chapter 49.
[11] U. S. Patent 1,960,740.
[12] In the 18th century, a boat-load of platinum brought to Spain from the new world was ordered sunk as valueless. The earliest record of the incident discovered to date is one in Diderot and d'Alembert's "Encyclopédie ou Dictionnaire raisonné de Sciences," published 1778; tome XXV, p. 187: "On assure que le roi d'Espagne a fait fermer ces mines (de Santaje et de Popayan) et a fait jeter à la mer une très grande quantité de platines pour prévenir les abus que ses sujets en faisoient."
[13] Phosphorus, arsenic, and bismuth compounds, alkali cyanides and sulfides, carbon from a smoky flame, attack platinum.
[14] Chapter 1.
[15] Alluvial deposits are secondary deposits; the original platinum-bearing rock has weathered and has been moved by water.

TABLE 166.—*Worlds production of platinum and other platinum group metals in troy ounces—1946.**

	(a) Platinum	(b) Other platinum metals	(a) and (b)
U.S.S.R. placer platinum	175,000	—	—
Canada, from refineries	130,400	114,200	—
Colombia, placer platinum	43,835	—	—
Union So. Africa, platinum concentrates	51,800	—	—
U. S., placer platinum**	22,949	2,808	—
Total (estimate)			576,000

* Minerals Yearbook.
** 22,882 ounces from Alaska.

1935. The 1946 production was surpassed in 1940, when it was 35,000 ounces.

The Russian production comes from the Ural Mountains, where there are several districts; the most important ones at the present time are those of the two rivers, the Iss and the Wija, which combine to form the Tura. The gravels of the river beds carry the platinum values over a distance of about 90 miles. The recovery is by hand panning, or by placer mining.

The platinum produced in Colombia is mainly a by-product of gold production, by panning or placer mining. Platinum is also recovered in the process of refining copper (Anaconda) and nickel ores.

The Russian crude platinum contains iron; nearly all platinum from placer mining carries iridium, and some also osmium, palladium, and other impurities. Iron is removed by hydrochloric acid. Platinum, palladium, and iridium may be separated by solution in aqua regia and heating the chlorides formed to 125° C.; from the solution of the resulting chlorides, ammonium chloride precipitates the platinum. It is reduced to platinum black, which is fused in the electric furnace or in the hydrogen-oxygen flame to the metal. The platinum prepared in this way retains about 2 per cent iridium, which is desirable, for the iridium hardens it.

The precious metals must be melted in the course of the manufacture of sheets, foils, wires, and shapes of various kinds, in order to form alloys of suitable compositions, or for remelting the cuttings and end-pieces, or for a purification. This may be done in an induction furnace, rapidly, and without danger of contamination by even gaseous fuel. The induction furnace [16] consists of a fire-clay crucible, for example, 3 inches in diameter, which is set in a coil of one-fourth inch iron pipe through which cold water circulates, plastered with asbestos mud in which the primary winding is placed. The metal scrap in the crucible is the secondary. A current of 250 volts (15 kilowatts) is transformed to 8000 volts in a transformer with reactance, and delivered to a condenser with a discharge gap; a frequency of 30,000 to 50,000 cycles (per second) is obtained. On connecting the primary, the metal begins to glow in a few seconds, and melts in 2 minutes or so, while the crucible remains cold to the touch. The liquid metal is violently agitated by the induced current.[17] A temperature of about 5500° F. (3038° C.) may be attained. By placing the crucible and furnace under a glass bell-jar

[16] The practice at the Williams Gold Refinery Works, of Buffalo, N. Y.
[17] The order in which the metals melt in the induction furnace is the order of their resistivity; the higher it is, the faster the metal melts.

and connecting it to a strong suction pump, occluded gas may be completely removed, an important precaution in materials for dental alloys.

The usual method of melting platinum is to place the metal pieces in a cavity in a two-piece block of lime, and to introduce the oxy-hydrogen flame (or the oxygen-gas flame) through an opening in the upper half of the lime block; the necessary high temperature, 3191° F. (1755° C.), the melting point of pure platinum, is thus reached.

In 1946, 234,479 ounces of platinum were sold to domestic consumers, of which 61 per cent went to jewelers, 13.3 to the chemical industry (for contact catalysis, for linings, nozzles, thermocouples, and furnace windings), 14.9 to the electrical industry, and 9.3 to dental and medical groups. 217,181 ounces of palladium were sold to consumers. Osmium, iridium, rhodium and ruthenium, amounted together to 32,915 ounces sold to consumers.

Radium and Uranium

Radium was originally concentrated from pitchblende or uraninite, a uranium oxide found in the Joachimsthal, in the northwestern part of Czechoslovakia. In the United States, it was concentrated in Pittsburgh, from Colorado carnotite, a sandstone impregnated with uranium vanadate. For a number of years, the American mines and plants were not operated, because their ores could not compete with the high grade ores discovered and soon actively mined in the Katanga region in the Belgian Congo (1923). A few years later, the Katanga ore was in turn surpassed and partly displaced by Canadian ore, from the area near Great Bear lake in the Arctic (Northwest Territories, Mackenzie District). The discovery of pitchblende deposits on LaBine Point in 1930, revealed as the main deposit a vein 1400 feet long which contained 62 per cent U_3O_8. Much of the Canadian ore contains leaf silver; some contains also rhodochrosite, a manganese carbonate; other veins are high in silica and free from carbonates. The richness of the ore may be illustrated as follows: there were required 128 tons of carnotite to produce one gram of radium, 30 to 40 tons of the Katanga ore, and only $6\frac{1}{2}$ to 10 tons of Great Bear ore to produce the same amount. Theoretically, a 100 per cent U_3O_8 ore contains 1 gram of radium in 4 tons. The Great Bear ore is shipped 1600 miles by boat to Edmonton and thence 2200 miles by rail to Port Hope, on Lake Ontario, for refining.

The method of recovering radium and uranium is to concentrate the ore, roast the crushed concentrate with salt, reduce it, leach it with hot sulfuric acid, and add barium chloride. The radium precipitates with the barium, lead and silver; the uranium is in solution. The precipitate is boiled with soda ash to form the carbonates; these are filtered, and on treatment with hydrochloric acid, radium and barium dissolve, and are made into the double bromide. Fractional crystallization gives radium bromide with 90 to 95 per cent $BaBr_2$. Radium bromide is a white solid, soluble in water. The uranium solution gives a sodium uranate, or oxides or other salts.

Radium salts are used for their radioactivity in the treatment of disease, especially carcinoma. Radium salts are also used in luminous paints mixed with intensifying admixtures such as zinc sulfide or calcium sulfide. Indus-

trial gamma-ray radiography in the non-destructive testing of metals is a well developed practice. The radium salt (say 200 milligrams of radium) in a pear-shaped container of lead, with windows, is placed at one face of the casting or other piece, a photographic film at the opposite one. The shadowgraph obtained is studied for defects. To these many uses for radium there is now added its use in generating neutrons, by allowing its emitted alpha ray to enter the beryllium nucleus.

FIGURE 346.—After 93 men in the mines at Great Bear Lake have worked two weeks to produce many tons of ore; after 160 men in the refinery have worked another two weeks, the precious radium material has been reduced to the group of crystals in this single glass flask in the hands of a worker. (Courtesy of the Eldorado Mines, Canada.)

Radium metal is rarely made; its salts, either as solids, or in solution, serve in its several applications. Uranium metal on the other hand is required, for use in the atomic pile for example; it is produced by electrolysis of potassium-uranium pentafluoride, or (later) that of uranium tetrafluoride. One of the four manufacturers of the metal produced 1000 pounds per week by end of 1942.

The extraction of radium always involved the study, and frequently the recovery of uranium. In the twenties and thirties, uranium salts were available at very moderate cost and were used, among other applications, as a source of weak (compared to radium) radioactivity. This activity had its source in the U_{235} isotope, which is present in the natural uranium in the ratio to the normal atomic mass, U_{238}, of 1 to 140. The radioactivity of U_{235} includes the emission of a neutron, a particle with mass 1, and without electrical charge, so that it can approach and enter a charged nucleus with comparatively great ease. The neutron characteristics were not well established until 1932.

Uranium metal, oxide and salts as by-products of the radium industry remained of secondary importance, until, at the beginning of the European phase of World War II, it became clear in the minds of nuclear scientists that it should be possible to collect (later to produce) enough neutron-sensitive uranium isotope to produce an explosive many times more powerful

than the standard chemical explosives. U_{235} was isolated by laborious, tedious physical means of separation [18] from U_{238}, and made into the bombs which were dropped on Hiroshima and Nagasaki. Early in 1940, it was discovered that U_{238} could be transformed by a series of nuclear reactions involving absorption and emission of fundamental atomic particles, into plutonium, a new element, number 94, and not an isotope of uranium. The conversion is partial, and after it has taken place, the newly formed plutonium is separated from the residual, unchanged uranium by chemical means

FIGURE 347.—The site of the radium ore deposit and the mining camp, Eldorado Mines, in 1937, seven years after the discovery. Great Bear Lake, Point LaBine, Mackenzie, Canada. (Eldorado Mines, Canada.)

In these sub-Arctic hills, 26 miles from the Arctic Circle, on the shores of Great Bear, the largest freshwater lake lying wholly within the British Empire, the richest known deposit of radium lay concealed for many centuries. In 1930, Gilbert LaBine discovered the pitchblende veins (uraninite) which contain not only radium, but its more important parent substance, uranium.

which are faster and simpler. Plutonium it should be remembered is a new element with chemical properties of its own. The nuclear reations are:[19]

$$_0n^1 + {}_{92}U^{238} \rightarrow {}_{92}U^{239};\ {}_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}e^0;\ {}_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + {}_{-1}e^0$$

The original neutron may be produced by the action of the alpha particle from radium on beryllium:

$$_2Alpha^4 + {}_4Be^9 \rightarrow {}_6C^{12} + {}_0n^1$$

or by other means, such as the spontaneous neutron emission. The energy of

[18] Minerals Yearbook, 1946, chapter on "Uranium and Thorium."

[19] The subscript preceding the atomic symbol is the charge on the nucleus or fundamental particle; the superscript following the symbol is the mass. U=uranium; Np=neptunium; Pu=plutonium; N=neutron, e=electron.

the neutron must be reduced considerably, which is accomplished by retarding its flight; it is slowed down, by means of graphite or heavy water.[19a]

Plutonium. In order to make plutonium, rods of natural uranium metal sealed in aluminum cans are placed in various positions inside a rectangular graphite column (such as 3′×3′×8′ in height). Neutrons (2.2 in number) generated by the spontaneous nuclear decomposition of an atom of U_{235} are retarded by reflection from the graphite crystals; the resulting slow neutrons penetrate the nucleus of some of the U_{238} atoms, producing through the steps indicated earlier, plutonium. The plutonium itself on capture of a slow neu-

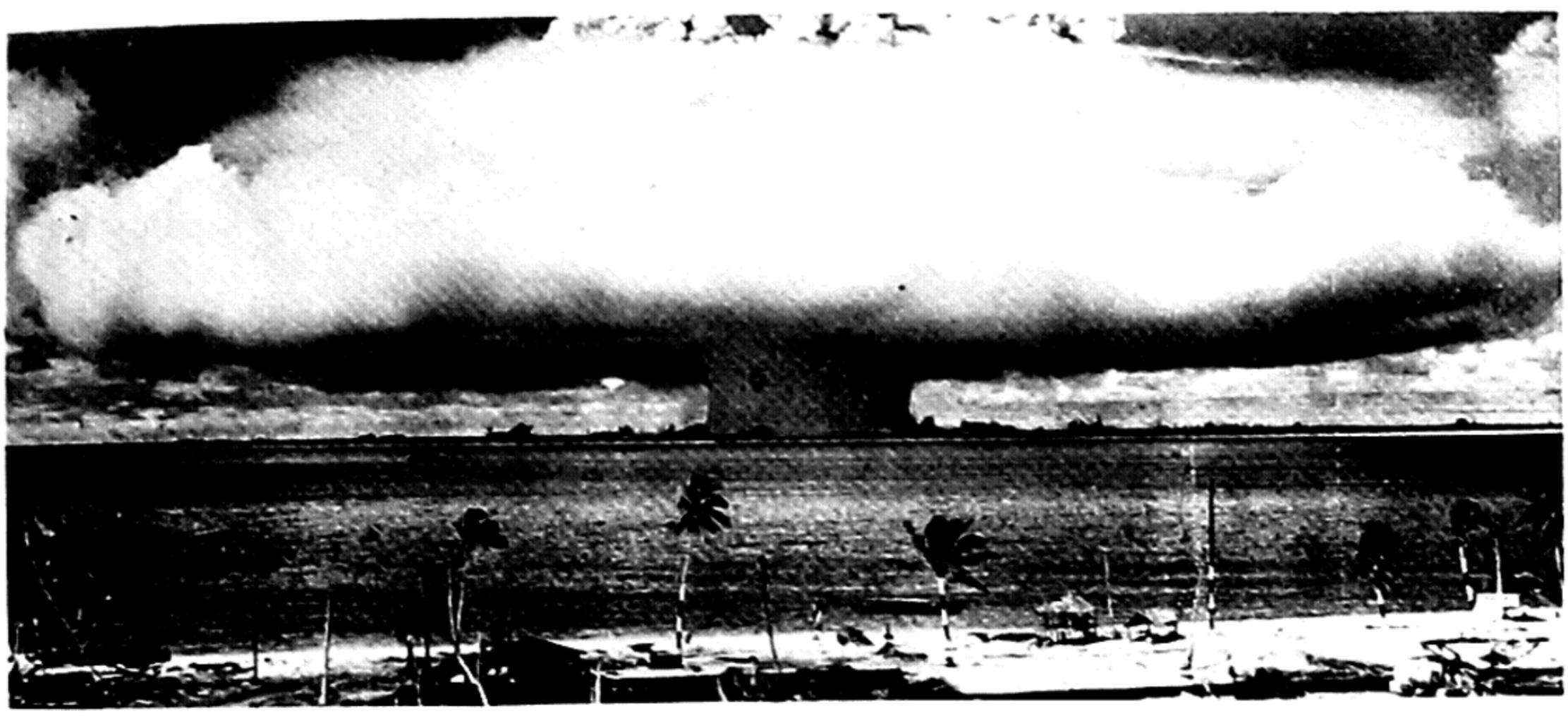


FIGURE 348.—Explosion of a plutonium bomb dropped from aeroplane over the water of the Bikini atoll, wherein a number of ships had been gathered for testing its effects. (Photograph by the Army Signal Corps.)

tron decomposes into smaller fragments, with a loss of mass which is converted into a considerable amount of energy. In its decomposition the plutonium itself generates a neutron which in turn acts on previously unattacked plutonium nuclei, so that the reaction once started, and with propitious disposition, continues after the fashion of a chain reaction. The graphite column in which these events take place is now a *self-sustaining chain-reacting pile.* The pile must be cooled, which is done by means of conduits in which water circulates, the water turning to steam under the proper conditions. This is the heat which it is sought to apply to useful purposes, and which then would justify the term of atomic fuel when applied to uranium.

The smaller nuclear fragments are radioactive, and their radiations (of gamma rays, electrons, and other) as well as that proceeding from the main nuclear changes must be arrested by shields, in order to protect personnel.

[19a] Heavy water is used in several of the atomic piles in Europe. These include Zoë. an experimental pile, at Fort Chatillon, near Paris, and a laboratory pile at Kjeller, near Oslo. In Canada, the Zeep pile at Chalk River, employs heavy water, as does also the N. R. X. pile in the same country. On the other hand, the Gleep pile at Harwell, England, employs graphite, as does also Bepo, also at Harwell. (Article by Peter Kihss, *N. Y. Herald-Tribune*, July 27, 1949).

Normally inactive chemical elements placed in the pile become temporarily radioactive and serve many useful purposes of study.

Thorium may be transformed into U_{233}, which upon capture of a slow neutron is fissionable; it is subject to similar strict Government regulations.

The atomic bomb remains a strict military secret so that its discussion is not possible. From published material, it is known that the nuclear decomposition of plutonium or of U_{235} is governable as long as a critical size is not reached. Once reached and exceeded, the decomposition takes on the char-

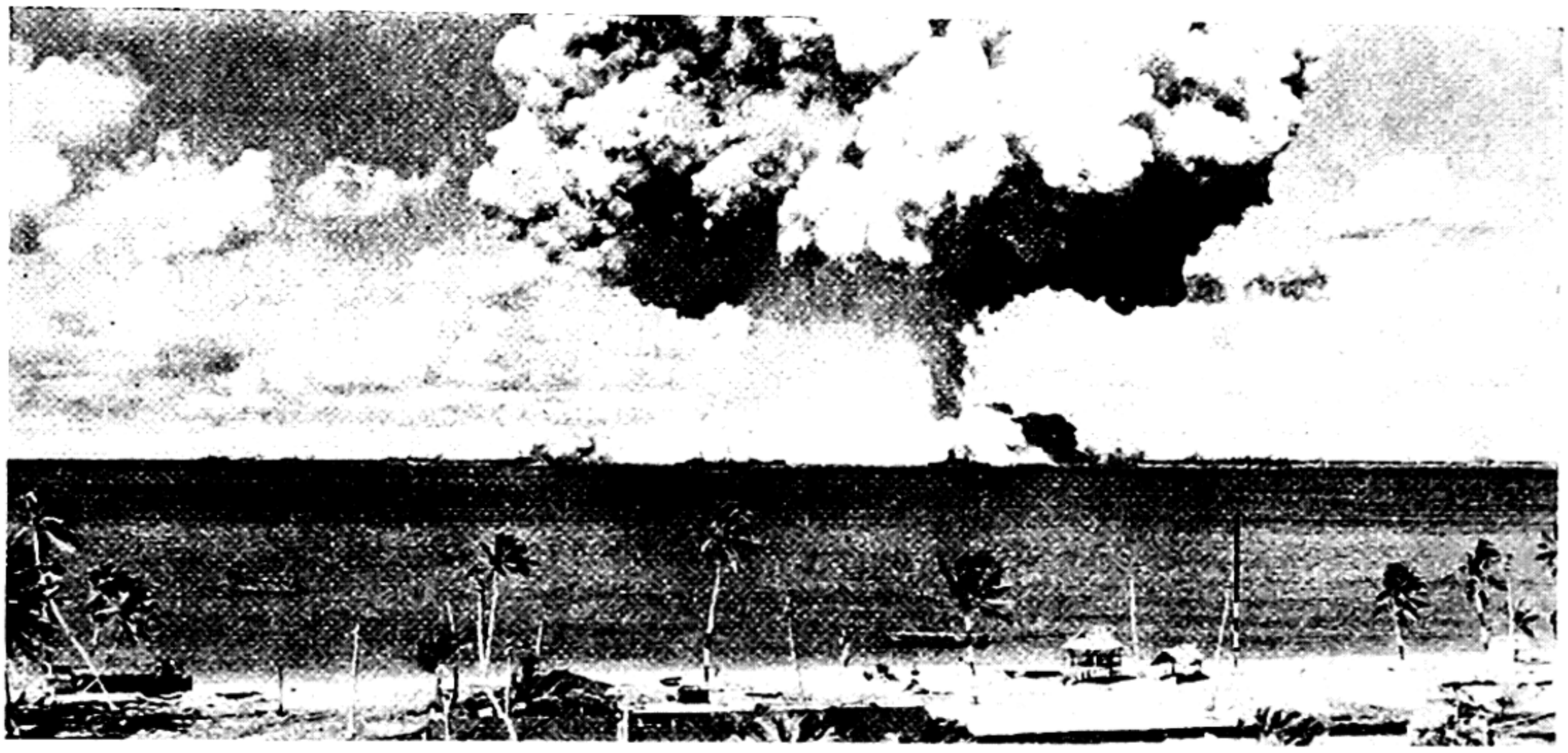


FIGURE 349.—A second view of the same explosion at Bikini, a few moments after the first picture was taken. (Photograph by the Army Signal Corps.)

acter of an explosion, superlatively destructive. The critical size was estimated in 1945 in the following language: "The mass of U_{235} required to produce explosive fission under appropriate conditions can hardly be less than 2 kilograms nor greater than 100 kilograms."[20]

The Atomic Energy Act of 1946 limits ownership of any facility for the production of fissionable material to the Commission created by the Act.[21] The Commission also controls the source material, its transportation and distribution.

TUNGSTEN

Tungsten in the United States is obtained chiefly from scheelite a tungstate of calcium, mined in Nevada. The main producing countries of the world are, in the order of their importance (partly potential): Kiangsi province, China; Burma; United States; Malay States; Portugal.

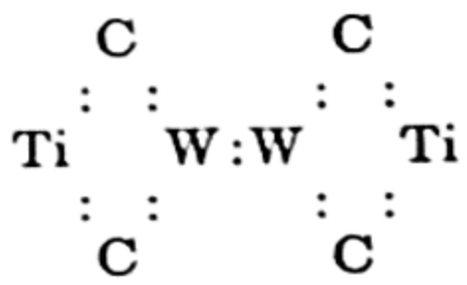
Ferrotungstate is manufactured, and also the metal, by forming the tungstic acid, calcining, and reducing with carbon. Tungsten filaments may be made from the metal mixed with sugar, and drawn into a wire which is then heated in an atmosphere of hydrogen; they may also be made by the

[20] "Atomic power," a Science Service publication, September 1945, p. 31.

[21] An abstract of the Atomic Energy Act will be found in Minerals Yearbook 1946, in the chapter "Uranium and Thorium."

substitution process, in which a carbon filament is heated in an atmosphere of tungsten oxychloride mixed with hydrogen. Tungsten is required for making the carbide, which is used as a cutting tool, for sand blast nozzles, and wire drawing dies.

Tungsten carbide, and similarly tungsten-titanium carbide, are made in carburizing furnaces at temperatures exceeding 4200° F. Carbide grains and powdered cobalt are ball milled to reduce particle size and to mix thoroughly, then extruded into shapes, and sintered at 2650° F. Heavy shrinkage takes place during sintering. The carbide shape is mounted on the edge of a steel form and becomes the cutting edge. There are various grades of tungsten carbide tools, each adapted to a certain duty (Carboloy, Kennametal, Tecco).[22] Kennametal contains tungsten-titanium carbide with formula $(WTiC_2)_2$:



Tungsten-titanium carbide

It is synthesized from tungsten, titanium and carbon, heated together in a nickel bath at high temperature; after cooling and digestion in acid fine steel-colored particles of the new carbide are obtained. The hard crystals with tungsten carbide, cobalt and other ingredients are made into carbide blanks by powder metallurgy, heating in an electric vacuum furnace.

Steel, brass, nickel, or silver articles may be tungsten plated in an alkaline solution containing dissolved tungstic oxide (WO_3) with 1 per cent of its weight of nickel in solution.[23] Without the nickel, the deposition of tungsten stops after a very thin layer has formed, through self-polarization. The article to be plated is made the cathode, while the anode may be platinum.

In 1946, 4,671,042 pounds of tungsten in the form of ores and concentrates were produced in the United States, while the general imports were 6,811,099 pounds; in 1947, 3,026,470 pounds in the form of ores (U. S.) were produced, which was 26.5 per cent of the corresponding 1943 figure. Of the 1946 consumption of tungsten 28 per cent were alloyed with steel, and 37 per cent were made into tungsten powder.

During World War II, tungsten was declared a strategic metal, and supplies were allocated; also the Defense Plant Corporation operated a chemical plant for tungsten at Salt Lake City, until late in 1946.

Thorium and Cerium

The Welsbach mantle[24] for gas light consists of thoria, ThO_2, and 1 or 2 per cent ceria, CeO_2, obtained from monazite sand found in Brazil (the best) and North Carolina and West Virginia. In order to extract thoria and ceria, the sand, washed free from earth, is freed from iron by passing it over electromagnets with low current, from garnet by the same electromagnets

[22] Made respectively by Carboloy Company, Detroit 32, Mich., Kennametal, Inc., Latrobe, Pa., and Tungsten Electric Corp., Union City, N. J.

[23] U. S. Patents 1,885,702; 1,885,701; 1,883,235.

[24] The Welsbach plant at Camden, N. J.

with high current. The remaining material is treated with sulfuric acid and from this solution the oxalates are precipitated; thorium oxalate is separated by solution in ammonium oxalate, in which cerium oxalate is not soluble. Both are refined further and transformed into the nitrates; these are dissolved and mixed to give the relative amounts corresponding to the figures above. In order to make the mantle, a weave of cotton or rayon is soaked with the solution of the nitrate mixture, dried, and ignited. The resulting shape consists of the oxides; it is dipped in collodium to stiffen it for transport. Soft mantles are also made. The Welsbach mantles are less important than forty years back; they will probably always remain of some importance for lighting in isolated places, such as lighthouses on the seacoast.

After the thorium salts are removed, and some of the cerium, there is obtained as a by-product a mixture of the salts of cerium, lanthanum, didymium, yttrium, and samarium. These salts are changed to the chlorides, and placed, gradually, in an iron crucible forming the cathode, in which a carbon anode dips. The crucible is heated just at the bottom to fuse the chlorides. There is obtained a button on the bottom of the crucible consisting of cerium with the other metals named as admixtures. The button is alloyed with 30 per cent iron and made into small pieces one-eighth inch in diameter and 1 inch long, mounted for cigar-lighters and gas-lighters. When the alloy is scratched with a piece of iron or flint, sparks are produced; this is the pyrophoric alloy.[25]

Thorium as an atomic fuel has been mentioned under uranium.

Metallic thorium has been prepared, although not on an industrial scale; a very complete reference is given below.[26]

Vanadium

The mine shipments of ores and concentrates (domestic) in 1946 were 1,272,148 pounds of contained vanadium, while the imports of ores and concentrates were 791,057 pounds. In the following year, the domestic production of vanadium ores rose to 3,026,470 pounds. The demand had shrunk considerably from that during the war years, when extraordinary means were taken to recover every possible vanadium-containing material;[27] in 1943, the best year, domestic mine shipments were 5,586,492 pounds, the imports of ores and concentrates 2,052,620 pounds of contained vanadium. One of the foreign ores is patronite, a sulfide of tungsten found in Peru not far from the Cerro de Pasco copper deposits. The consumption of vanadium

[25] U. S. Patent 1,273,223; compare also *Ind. Eng. Chem.*, 10, 849 (1918).

[26] "Metallic thorium," J. W. Marden and H. C. Rentschler, *Ind. Eng. Chem.*, 19, 97 (1927).

[27] During the recent World War in the years 1940 to 1945 323 tons of vanadium were salvaged from 3000 tons of petroleum residues. These ashes were left from the combustion of 3,000,000 tons of oil, partly from oil-fired vessels of the Royal Navy and Merchant Navy, mainly from oil burning plants in Great Britain and South America. Top production came from Shell refinery at Curacao which in 1944 turned out about 70 per cent of the Shell group's total production of vanadium. The remainder for that year were due 10 per cent to the Admiralty, 15 per cent to the Merchant Navy, 5 per cent to South American and U. K. power plants. *Synthetics and By-Products*, September 1945, 7, p. 297-300.

is in the manufacture of high speed steel (52.4 per cent of the 1946 consumption) and other tool steel and alloy steel, and for special purpose non-ferrous alloys (Hastelloy B). Chemically, vanadium resembles tantalum, and not antimony and bismuth.[28] The price for ferro-vanadium was $2.75 to $2.90 per pound of contained vanadium.

Other Patents

U. S. Patent 2,029,387, agent to improve the metal deposit from a plating bath; U. S. Patent 2,425,573, on an improved method for extracting thorium from minerals containing it, separating cerium at the same time, to Dr. Frederick Soddy, the discoverer of isotopes.

Reading References

"The mineral industry during 1935," edited by G. A. Roush, New York, McGraw-Hill Book Co., 1936. Published annually.

"The commercial production and uses of radium," Charles H. Viol, *J. Chem. Educ.*, 3, 757 (1926).

"The metallurgy of non-ferrous metals," Wm. Gowland, London, Chas. Griffin and Co., Ltd., 1918.

"Vanadium and some of its industrial applications," J. Alexander, *J. Soc. Chem. Ind.*, 48, 871-8, 895-901 (1929), contains a bibliography.

"Mesothorium," Herman Schlundt, *U. S. Bur. Mines T. P.* 265 (1922).

"Radium and uranium from Great Bear Lake ores," *Can. Chem. Met.*, 17, 251 (1933).

"Radium preparation and uses," J. D. Leitch, *Can. Chem. Met.*, 20, 342 (1936).

"Gamma ray radiography in the non-destructive testing of metals," published by Canadian Radium and Uranium Corporation, Rockefeller Center, New York.

"The Goodnews platinum deposits, Alaska," J. B. Mertie, Jr., *Geol. Survey Bull.* 918, 1940.

"Silver in Industry," edited by Lawrence Addicks, New York, Reinhold Publishing Corp., 1940.

"Minerals Yearbook, 1946," published by the Bureau of Mines, Dept. of the Interior, obtainable from Superintendent of Public Documents, Washington 25, D. C.

[28] *Ind. Eng. Chem.*, 19, 787 (1927), J. W. Marden and M. N. Rich.

Appendix

Table of the More Important Chemical Elements with Their Symbols and Atomic Weights

(From the International Table of Atomic Weights for 1947)

Aluminum	Al	26.97	Mercury	Hg	200.61
Antimony	Sb	121.76	Molybdenum	Mo	95.95
Argon	A	39.944	Neon	Ne	20.183
Arsenic	As	74.91	Nickel	Ni	58.69
Barium	Ba	137.36	Nitrogen	N	14.008
Beryllium	Be	9 02	Osmium	Os	190.2
Bismuth	Bi	209 .0	Oxygen	O	16.000
Boron	B	10.82	Palladium	Pd	106.7
Bromine	Br	79.916	Phosphorus	P	30.98
Cadmium	Cd	112.41	Platinum	Pt	195.23
Calcium	Ca	40.08	Plutonium	Pu	239.
Carbon	C	12.01	Potassium	K	39.096
Cerium	Ce	140.13	Radium	Ra	226.05
Cesium	Cs	132.91	Radon	Rn	222.
Chlorine	Cl	35.457	Rhodium	Rh	102.91
Chromium	Cr	52.01	Rubidium	Rb	85.48
Cobalt	Co	58.94	Selenium	Se	78.96
Columbium	Cb	92.91	Silicon	Si	28.06
Copper	Cu	63.57	Silver	Ag	107.880
Fluorine	F	19.0	Sodium	Na	22.997
Gold	Au	197.2	Strontium	Sr	87.63
Helium	He	4.003	Sulfur	S	32.06
Hydrogen	H	1.008	Tellurium	Te	127.61
Iodine	I	126.92	Thorium	Th	232.12
Iridium	Ir	193.1	Tin	Sn	118.70
Iron	Fe	55.85	Titanium	Ti	47.90
Krypton	Kr	83.7	Tungsten	W	183.92
Lanthanum	La	138.92			full value
Lead	Pb	207.21	Uranium	U	238.07
Lithium	Li	6.940	Vanadium	V	50.95
Magnesium	Mg	24.32	Zinc	Zn	65.38
Manganese	Mn	54.93	Zirconium	Zr	91.22

Table for Conversions

1 meter = 39.37 inches
1 foot = 304.80 millimeters
1 inch = 25.40 millimeters
1 pound = 453.6 grams
1 square meter = 10.7631 square feet
1 ounce avoirdupois = 28.35 grams.
1 ounce troy = 31.10 grams.

1 cubic foot = 28.315 liters; 1 cubic foot of water at 62° F. weighs 62.321 pounds.
1 cubic foot contains 7.48 gallons (U. S.); 1 cubic meter = 35.3166 cu. ft.
1 gallon (U. S.) of water weighs 8.33 pounds.
1 gallon (English) of water weighs 10.0 pounds.
1 kilometer = 0.6214 mile.
1 gross ton = 1 long ton = 2200 pounds.
1 short ton = 1 net ton = 2000 pounds.
1 metric ton = 1000 kilograms = 2205 pounds.

1 gram mole of a gas at S.T.P. = 22.4 liters = 0.791 cubic foot.
1 $\mu = 10^{-6}$ meter $= 10^{-4}$ centimeter $= 10^{-3}$ millimeter
1 $m\mu = 10^{-6}$ millimeter = 10 A.U.

To change centigrade degrees to Fahrenheit degrees, multiply by 9/5 and add 32.
The British Thermal Unit (Btu.) is the quantity of heat necessary to raise 1 pound of water 1° F. from 60 to 61°; it also equals 777.52 foot-pounds.
The large Calorie, also called the kilogram calorie (Cal), is the amount of heat necessary to raise 1 kilogram of water 1° C. from 17 to 18°.
1 Cal = 3.968 Btu. 970 Btu. are required to vaporize 1 pound of water at 212° F. to steam at 212° F.
The specific heat of water is 1.

---

1 horsepower = 0.7457 kilowatt.
1 kilowatt = 1.341 horsepower.
Horsepower and kilowatts require a time factor to mean a quantity of power.
1 horsepower-hour = 0.7457 kilowatt-hour.
1 horsepower-second = 550 foot-pounds.

---

1 pound pressure is equivalent to a column of water 2.304 feet high.
Normal atmospheric pressure at sea level is 14.70 pounds per square inch and supports a column of mercury 29.92 inches high at 15° C., or a column of water 33.93 feet high at 15° C., which is also the maximum lift on the suction side of a pump. 29.92 inches = 760 millimeters.

---

1 volt times 1 ampere equals 1 watt.
1000 watts equal 1 kilowatt.
1 ampere-second deposits 0.001118 grams of silver.

Note: The pound in this table is the avoirdupois pound in every case. Unless otherwise specified, this is the pound meant in ordinary affairs.

Tables on heat values of fuels and on specific gravities of metals and alloys, will be found in the text.

For calculation of costs, consult:
"The technical organization, its development and administration," John Morris Weiss and Charles Raymond Downs, McGraw-Hill Co., New York, 1914.

The value called p_H is a negative exponent of 10; 10 with that exponent, times 1, gives the number of hydrogen ions, in grams, in 1 liter of the solution. The range is from 0.0 to 14.0, 7.0 being the neutral point.

A cord of wood is a pile 8 feet long, 4 feet wide, and 4 feet high.

Specific Gravity Equivalents for Degrees Baumé for Liquids Heavier than Water

* Temperature 60°/60° F.
One gallon distilled water at 60° F. in air = 8.32823 lbs.
Table adopted by the U. S. Bureau of Standards from the formula:

$$\text{° Baumé} = 145 - \frac{145}{\text{Sp. Gr.}\frac{60°}{60°}\text{ F.}}$$

Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon	Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon
0.	1.0000	8.328	36.	1.3303	11.079
1.	1.0069	8.385	37.	1.3426	11.181
2.	1.0140	8.445	38.	1.3551	11.285
3.	1.0211	8.504	39.	1.3679	11.392
4.	1.0284	8.565	40.	1.3810	11.501
5.	1.0357	8.625	41.	1.3942	11.611
6.	1.0432	8.688	42.	1.4078	11.724
7.	1.0507	8.750	43.	1.4216	11.839
8.	1.0584	8.814	44.	1.4356	11.956
9.	1.0662	8.879	45.	1.4500	12.076
10.	1.0741	8.945	46.	1.4646	12.197
11.	1.0821	9.012	47.	1.4796	12.322
12.	1.0902	9.079	48.	1.4948	12.449
13.	1.0985	9.148	49.	1.5104	12.579
14.	1.1069	9.218	50.	1.5263	12.711
15.	1.1154	9.289	51.	1.5426	12.849
16.	1.1240	9.361	52.	1.5591	12.984
17.	1.1328	9.434	53.	1.5761	13.126
18.	1.1417	9.508	54.	1.5934	13.270
19.	1.1508	9.584	55.	1.6111	13.417
20.	1.1600	9.660	56.	1.6292	13.568
21.	1.1694	9.739	57.	1.6477	13.722
22.	1.1789	9.818	58.	1.6667	13.880
23.	1.1885	9.898	59.	1.6860	14.041
24.	1.1983	9.979	60.	1.7059	14.207
25.	1.2083	10.063	61.	1.7262	14.376
26.	1.2185	10.148	62.	1.7470	14.549
27.	1.2288	10.233	63.	1.7683	14.727
28.	1.2393	10.321	64.	1.7901	14.908
29.	1.2500	10.410	65.	1.8125	15.095
30.	1.2609	10.501	66.	1.8354	15.285
31.	1.2719	10.592	67.	1.8590	15.482
32.	1.2832	10.686	68.	1.8831	15.683
33.	1.2946	10.781	69.	1.9079	15.889
34.	1.3063	10.879	70.	1.9333	16.101
35.	1.3182	10.978			

*All densities taken at 60° F. and referred to distilled water at 60° F. as 1.0000.

Degrees Baumé with Corresponding Specific Gravity for Liquids Lighter than Water *

$$\text{° Baumé} = \frac{140}{\text{sp. gr. } 60°/60° \text{ F.}} - 130, \text{ at } 60° \text{ F.}$$

Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon	Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon
10.0	1.0000	8.328	55.0	0.7568	6.300
11.0	.9929	8.269	56.0	.7527	6.266
12.0	.9859	8.211	57.0	.7487	6.233
13.0	.9790	8.153	58.0	.7447	6.199
14.0	.9722	8.096	59.0	.7407	6.166
15.0	.9655	8.041	60.0	.7368	6.134
16.0	.9589	7.986	61.0	.7330	6.102
17.0	.9524	7.931	62.0	.7292	6.070
18.0	.9459	7.877	63.0	.7254	6.038
19.0	.9396	7.825	64.0	.7216	6.007
20.0	.9333	7.772	65.0	.7179	5.976
21.0	.9272	7.721	66.0	.7143	5.946
22.0	.9211	7.670	67.0	.7107	5.916
23.0	.9150	7.620	68.0	.7071	5.886
24.0	.9091	7.570	69.0	.7035	5.856
25.0	.9032	7.522	70.0	.7000	5.827
26.0	.8974	7.473	71.0	.6965	5.798
27.0	.8917	7.425	72.0	.6931	5.769
28.0	.8861	7.378	73.0	.6897	5.741
29.0	.8805	7.332	74.0	.6863	5.712
30.0	.8750	7.286	75.0	.6829	5.685
31.0	.8696	7.241	76.0	.6796	5.657
32.0	.8642	7.196	77.0	.6763	5.629
33.0	.8589	7.152	78.0	.6731	5.602
34.0	.8537	7.108	79.0	.6699	5.576
35.0	.8485	7.065	80.0	.6667	5.549
36.0	.8434	7.022	81.0	.6635	5.522
37.0	.8383	6.980	82.0	.6604	5.497
38.0	.8333	6.939	83.0	.6573	5.471
39.0	.8284	6.898	84.0	.6542	5.445
40.0	.8235	6.857	85.0	.6512	5.420
41.0	.8187	6.817	86.0	.6482	5.395
42.0	.8140	6.777	87.0	.6452	5.370
43.0	.8092	6.738	88.0	.6422	5.345
44.0	.8046	6.699	89.0	.6393	5.320
45.0	.8000	6.661	90.0	.6364	5.296
46.0	.7955	6.623	91.0	.6335	5.272
47.0	.7910	6.586	92.0	.6306	5.248
48.0	.7865	6.548	93.0	.6278	5.225
49.0	.7821	6.511	94.0	.6250	5.201
50.0	.7778	6.475	95.0	.6222	5.178
51.0	.7735	6.440	96.0	.6195	5.155
52.0	.7692	6.404	97.0	.6167	5.132
53.0	.7650	6.369	98.0	.6140	5.110
54.0	.7609	6.334	99.0	.6114	5.088
55.00	.7568	6.300	100.0	.6087	5.066

* Bureau of Standards, Circular No. 57.

*Degrees A. P. I. (American Petroleum Institute) and Corresponding Specific Gravity for Petroleum Oils, Mainly for Liquids Lighter Than Water, at 60° F. Referred to Water at 60° F.**

$$\text{Degree A.P.I.} = \frac{141.5}{\text{sp. gr. } 60°/60° \text{ F.}} - 131.5$$

Degrees A.P.I.	Specific Gravity 60°/60° F	Pounds per Gallon	Degrees A.P.I.	Specific Gravity 60°/60° F	Pounds per Gallon
10.00	1.0000	8.328	56.00	.7547	6.238
11.00	.9930	8.270	57.00	.7507	6.249
12.00	.9861	8.212	58.00	.7467	6.216
13.00	.9792	8.155	59.00	.7428	6.184
14.00	.9725	8.099	60.00	.6389	6.151
15.00	.9659	8.044	61.00	.7351	6.119
16.00	.9593	7.989	62.00	.7313	6.087
17.00	.9529	7.935	63.00	.7275	6.056
18.00	.9465	7.882	64.00	.7238	6.025
19.00	.9402	7.830	65.00	.7201	5.994
20.00	.9340	7.778	66.00	.7165	5.964
21.00	.9279	7.727	67.00	.7128	5.934
22.00	.9218	7.676	68.00	.7093	5.904
23.00	.9259	7.627	69.00	.7057	5.874
24.00	.9100	7.578	70.00	.7022	5.845
25.00	.9042	7.529	71.00	.6988	5.817
26.00	.8984	7.481	72.00	.6953	5.788
27.00	.8927	7.434	73.00	.6919	5.759
28.00	.8871	7.387	74.00	.6886	5.731
29.00	.8816	7.341	75.00	.6852	5.703
30.00	.8762	7.296	76.00	.6819	5.676
31.00	.8708	7.251	77.00	.6787	5.649
32.00	.8654	7.206	78.00	.6754	5.622
33.00	.8602	7.163	79.00	.6722	5.595
34.00	.8550	7.119	80.00	.6690	5.568
35.00	.8498	7.076	81.00	.6659	5.542
36.00	.8448	7.034	82.00	.6628	5.516
37.00	.8398	6.993	83.00	.6597	5.491
38.00	.8348	6.951	84.00	.6566	5.465
39.00	.8299	6.910	85.00	.6536	5.440
40.00	.8251	6.870	86.00	.6506	5.415
41.00	.8203	6.830	87.00	.6476	5.390
42.00	.8155	6.790	88.00	.6446	5.365
43.00	.8109	6.752	89.00	.6417	5.341
44.00	.8063	6.713	90.00	.6388	5.316
45.00	.8017	6.675	91.00	.6360	5.293
46.00	.7972	6.637	92.00	.6331	5.269
47.00	.7927	6.600	93.00	.6303	5.246
48.00	.7883	6.563	94.00	.6275	5.222
49.00	.7839	6.526	95.00	.6247	5.199
50.00	.7796	6.490	96.00	.6220	5.176
51.00	.7753	6.455	97.00	.6193	5.154
52.00	.7711	6.420	98.00	.6166	5.131
53.00	.7669	6.385	99.00	.6139	5.109
54.00	.7628	6.350	100.00	.6112	5.086
55.00	.7587	6.316			

* Bureau of Standards, Circular C 410.

DIESEL FUEL STANDARDS

The following specifications for Diesel Oils are given because these fuels are comparatively new, and it is difficult to find specifications for them in the usual collections.

Criteria of Diesel Fuels, Their Relatiue Importance, L. J. Le Mesurier, Anglo-Iranian Oil Co. Petroleum Times 37, *85 (1937), Jan. 16.*

Following are three specifications that have been considered by the British Standards Institution:

"Grade A—For automotive or other similar types of engines with small cylinders. Speed above 800 r.p.m. and high standard of performance essential.

"Grade B—For medium speed engines and powers not less than 25 b.h.p. per cylinder. For example, industrial units and main and auxiliary marine engines.

"Grade C—For large slow-running engines where adequate provision is made for heating and cleaning the fuel.

Grade		A	B	C
Flash point	Minimum	150° F.	150° F.	150° F.
Aniline point*	Minimum	60° C.	45° C.	...
Hard asphalt	Maximum	0.01%	2.0%	4.0%
Conradson carbon	Maximum	0.2%	4.0%	8.0%
Ash	Maximum	0.01%	0.05%	0.10%
Viscosity redwood No. 1 at 100° F.	Maximum	45"	100"	750"
Pour Point	Maximum	20° F.	...	
Sulfur content	Maximum	1.0%	2.0%	1.0%
Water content	Maximum	Not to exceed 0.1%	0.5%	1.0%
Distillation, Vol. to 350° C.	Minimum	85%	...	...
Calorific value, gross	Minimum	19,250	18,750	18,250

*Approximate measure of ignition quality pending the development of a standard engine test."

Navy Department Specification for Diesel Fuel. Specification No. 7-0-2c August 1, 1936.

"B. Grade B-1. Fuel oil for Diesel engine shall be furnished in one grade only.

"C. Material and Workmanship, etc. C-1. Diesel fuel oil shall be a petroleum distillate. It shall be free from grit, acid, and fibrous or other foreign matter likely to clog or injure pumps, nozzles, or valves.

"E. Detail Requirements. E-1. Fuel oil for Diesel engines shall conform to the following chemical and physical characteristics:

Test	Test No. F. S. B.	Test No. A. S. T. M.	Limit
Flash point, closed cup, °F., minimum	110.22	D93–22	150
Pour point, °F., maximum	20.14	D97–33	0
Viscosity, SSU, at 100° F.	30.43	D88–33	35–45
Water and sediment, per cent, maximum	300.32	D96–30	0.05
Total sulfur, per cent, maximum	520.22	D129–33	1.0
Carbon residue, per cent, maximum	500.13	189–30	0.2
Ash, per cent, maximum	542.1	.....	0.01
Corrosion at 212° F., copper strip	530.31	.....	(1)
90 per cent distillation temperature, °F., maximum	100.14	D86–30	675
Diesel index number, minimum	.....	.....	(2)45
A.P.I. gravity	40.1	D287–33	
Aniline point	310.11		

(1) Negative. (2) See F-4.

"F. Methods of Sampling, Inspection, and Tests.

F-1. Sampling.—Samples shall be taken according to the procedure described in Section F of Federal Specification VV-L-791, referred to in Section A.

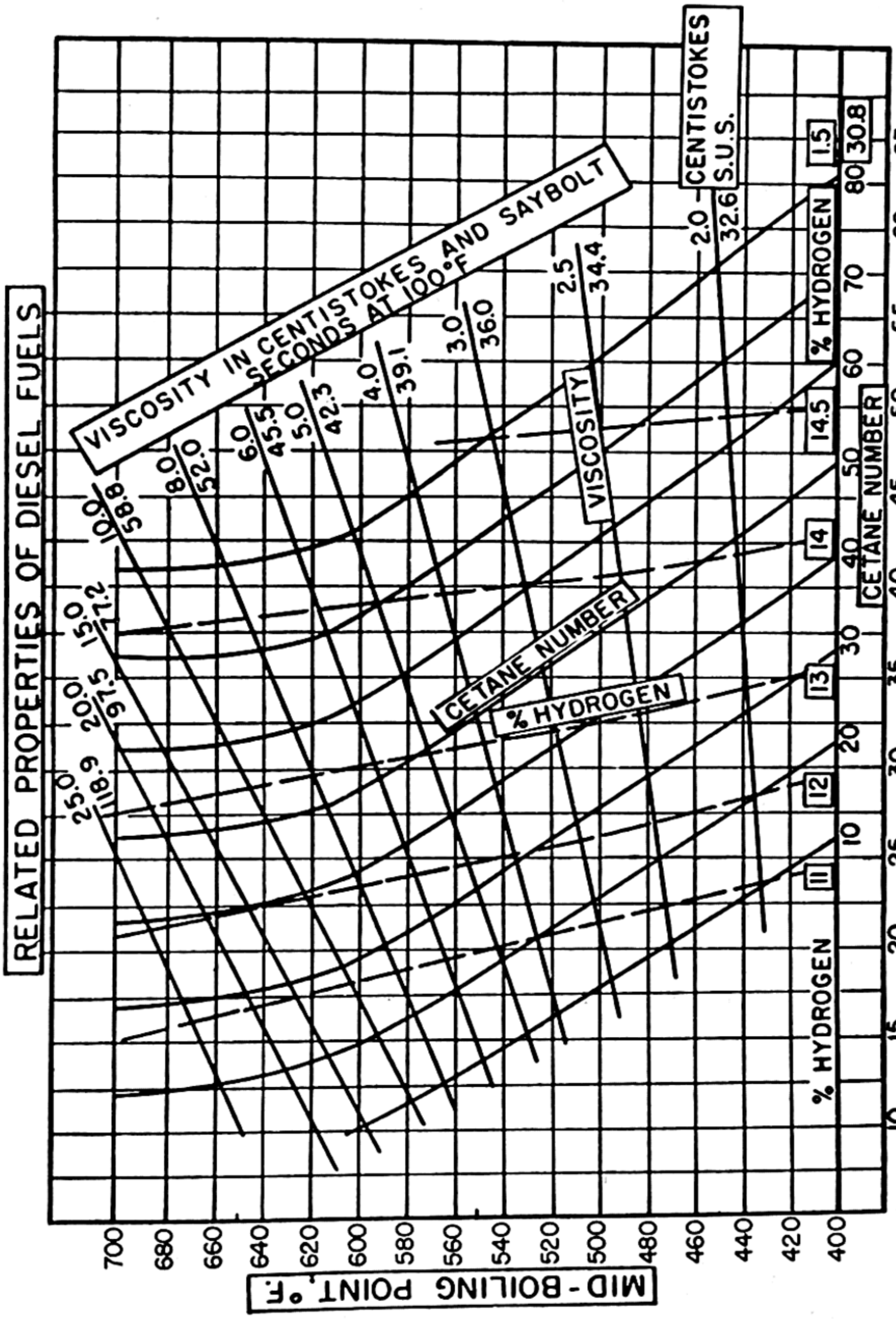
F-2. Inspection and tests.—Unless otherwise specified, all tests shall be made according to the methods for testing contained in section F of Federal Specification VV-L-791.

F-3. Diesel index number.—The Diesel index number shall be determined by the following equation:

$$\text{Diesel index number} = \frac{\text{aniline point (°F.)} \times \text{A.P.I. gravity}}{100}$$

The aniline point shall be determined in °F. by the method described as part of method 310.11, Federal Specifications VV-L-791.

F-4. In the event that the fuel supplied fails to exhibit satisfactory ignition quality in use, the right is reserved to require, in lieu of the minimum Diesel index number of 45, a minimum cetane number of 45, as determined in the C.F.R. turbulent-head type fuel-testing engine by the knockmeter delay method."



The related properties of Diesel fuels. [Courtesy of the Standard Oil Company (New Jersey)].

Index

(When more than one page reference is given, the references are arranged in the order of their importance)

A

Abietic acid, 311, 743
Abrasives, 334
Accelerators, 817
Acetaldehyde, 319, 534, 656
Acetate of lime, 322
Acetate rayon, 455
Acetic acid,
  Brewster process, 323
  by fermentation, 414
  from wood, 317
    direct, 322
    indirect, 319
  glacial, 536, 456
  synthetic, 533, 535
Acetic anhydride, 325, 534, 536
Acetol acetate, 317
Acetone, 317, 324, 410, 413,
  synthetic, 325, 534
Acetyl methyl carbinol, 654
Acetylation, 456
Acetylsalicylic acid, 656, 657
Acetylene (Ethyne),
  chemistry of, 534, 538
  derivatives, tables, 534, 537
  generation of, 387, 389
  industrial gas, 387
Acid Alizarine Black, 604
Acid dyes, 569
Acid egg, 5
Acids, *see* specific names
Acridine Yellow, 614
Acrospire, 400
Acrylate resins, 746
Acrylic acid, 540
Acrylonitrile, 540
Activated alumina, 900
Activated carbon, 317
Activated charcoal, 726
Activated sludge process, 271
Adhesives, 769, 743
Adipic acid, 460, 462, 464
Adhesives, 769
Adiponitrile, 463, 464
Adsorbents, for vapors, 465
Aerosols, 793
Agent M, 702
Air conditioning, 914
Aircraft fuel, 100 octane, 515
Alcohol, absolute, 407
  benzene process, 407
  glycerin process, 409
Alcohol, ethyl, 395
  absolute, 407
  denatured, 405
Alcohol, ethyl,
  industrial, 395, 403
  source materials, 404, 316
  synthetic, 403
  and *see* Industrial alcohol
Alcohol from molasses, 396
Alcoleter, 528
Alcotate, 405
Aldehol, 405
Algol Yellow, 618
Alizarine dyes, 594, 615, 616
Alizarine Sapphire B, 616
Alizarine Sapphire A, 616
Alizarine Cyanine Green GEx, 616
Alkali cellulose, 450
Alkaline fusion, 580, 592, 615
Alkyd resins, 741, 743, 683
Alkylation, 580, 591, 516
Alkylation process, for gasoline, 516
Alloys, 972
Allyl alcohol, 701
Allyl chloride, 700, 701
Aloxite, 338
Alrosene PD, 702
Alsorept, 702
Alum, 52
  ammonia, 54
  filter, 52, 255, 257
  potassium, 54
  sodium, 53
Alum floc, 257
Aluminum, 346
Aluminum alloys, 351
Aluminum bronze, 352
Aluminum oxide,
  bauxite, 52, 338, 347
  crystals, 338
  furnace, 339
  fused, 338
Aluminum sulfate, 52
Alundum, 338
Alunite, 156
Amaranth, 602
Amate, *see* Ammonium sulfamate
Ambergris, 652
Amberlite IR-4B, 266
American continuous disk suction filter, 862
Ameripol, 814
Ammonia,
  anhydrous, 120
  natural, extraction, 281
  natural, distillation, 294
  refrigerant, 242
  synthetic, 114
  uses, 124

Ammonia aqua, 294
Ammonia, direct synthetic, process,
American, 116
Casale, 123
Claude, 122
Haber, 120
Mathieson, 115
Mont Cenis, 122
Ammonia oxidation, 126, 127, 128
Ammonia soda process, 58
Ammonia still, 294
Ammoniated urea solution, 149
sodium nitrate solution, 149
Ammonium nitrate, 149, 150
Nitraprills, 150
Ammonium persulfate, 360
Ammonium phosphate, 143
diammonium, 143
Ammonium sulfamate, 793
Ammonium sulfate, from coal,
crystal process, Wilputte, 282
direct formation, 281
yield, 284
Ammophos, 143
Amyl alcohol,
natural, 401
synthetic, 413
Amylase, 400
Anhydrous bisulfite of soda, 86
Animal oils and fats, 639, 635
Aniline, 584, 588, 591, 594, 595
Ansco Color Film, 779
Ansco Printon, 781
Anthracene, 290, 580, 562
Anthaquinone, 594, 593, 584, 562
Antibiotics, 658
Antifreeze, 317, 320
Antiknock compounds, 514
Antu, 794
Appliances used by the Chemical Engineer, 844 853, 866, 879
Aralac, Aratex, 460
Argon, 384, 385
Aroclors, 748
Arsphenamine, 656
Artificial fog generator, 729
Ascoloy, 237
Aspirin, 656, 657
Asphalt, 523
Atabrin, 656
Atomic bomb, 988
Atomic hydrogen torch, 390
Atomic pile or reactor, 987
Auramine, 613
Automobile tires and tubes, 820
Aviation gasoline, 515, 516
Avitex C, 702
Azo dyes, 597
Azo Rubine, 602
Azoic dyes, 625

B

Babbitt, 973
Badger, Alfred E., collaborator, 194
Badische, sulf. acid process, 31
Bagasse, 474, 479, 482
Bakelite phenolic resin, 735
Baking enamels, 741
Baking powders, 143
Balata, 823
Banbury mixer, 819
Barium peroxide, 363
Bauxite, 52, 338, 347
Bayer process, 348
Beater, Hollander, 432, 433, 434
Beeswax, 642
Beet sugar, 468
Benzaldehyde, 591, 649
Benzene, 283, 290, 291, 292, 590, 581
Benzidine, 606
Benzoyl chloride, 358
Benzoyl peroxide, 358
Berl, Ernst, 12
Beryllium, 972, 986, 985
Bird-Young United Filter, 661
Birkett, Lionel S., collaborator, 468
Black powder, 716
Blackstrap, 478
Bleach, 107
Blowcase, 5
Blue Coal, 229
Board, paperboard, 431
Boards, laminates, canvas, 742
paper, 743
Boilers,
diphenyl, 231
diphenyl oxide, 231
mercury vapor, 240
steam, 229
Boilers,
fire-tube, 230
locomotive, 229
marine, 229
stationary, 229
water-tube, 229
Bookpaper, 431
Booth, Earl, collaborator, 645
Borax, 156, 155
Bordeaux B, 602
Bordeaux (red), 608
Bordeaux mixture, 797, 788
Boric acid, 156
Boron carbide, 341
Bosch, Carl, and Wilhelm Meiser, 159
Bottle seals, 465
Bottled gas, 305, 307
Brass, 973
Brewing industry, 405
Bricks, 894
building, 186
basic, 188
firebricks, 187, 319
insulating, 188, 319
neutral, 188
red, 186
refractories, 188
silica, 188
silicon carbide, 188
Brilliant Crocein M, 603
Brilliant Yellow, 610
British gum, 482
Brix scale, 480

Bromine, 75, 255
Bronze, 973
Bubble tower, 496
Bucket elevator, 879, 637
Buffalo municipal water filtration plant, 256
Buffalo sewage disposal plant, 270, 271
  sewage treatment, flowsheet, 271
  solids disposal, flowsheet, 272
Buffalo Black 10B, 604
Bunker oil, 519
Buromin, 232
Butadiene,
  from alcohol, 824
  from petroleum refinery products, 825
Butane, 512, 305
  isobutane, 512
Butter, 641
Butyl alcohol, 410
Butyl rubber, 810
Butyl stearate, 681
Butylene, 519
  isobutylene, 516
Butynediol, 439

C

Calcium acetate, 319, 325
Calcium arsenate, 788
Calcium carbide, 341, 111, 124
Calcium chloride, 64, 66, 65
  natural, 66
Calcium cyanamide, 124, 341, 111, 741
Calcium cyanide, 794
Calcium hydroxide, *see* Lime, hydrated
Calcium hypochlorite, 107, 108
  High Test Hypochlorite, 108
Calgon, 232
Camera, 776
Camphor, 756, 748
Cane sugar, 468
  direct consumption, 479
  refining, 479
Carbazol, 290
Carbohydrates, from wood, 313
Carbometer, 920
Carbon black, 671, 683
Carbon dioxide,
  fire extinguishers, 245
  fire foam, 245
  manufacture, 244, 393, 397, 412
  refrigerant, 242, 243
  solid, 245
Carbon disulfide, 343
Carbon monoxide, liquefied, 387
Carborundum, 335, 336
Carboxide, 794
Carboxylation, 540
Carnallite, 151
Carnauba wax, 642
Casale process, 123
Case-hardening, 953, 954, 952
Casein, 764, 750
Casein plastics, 750
Cassia oil, 649
Castings, iron, 892
Castings, steel, 894
Castor oil, 638, 750, 681
  dehydrated, 638
  soluble, 638
Catalysts, in paints, 673
Catalysts, solid, 554
  extrusion press, 556
  manufacture, 555, 552
  composition, 552, 511, 306
Catalytic cracking, 504
Catalytic reactions, tables, 557, 553
Catskill, Croton and Long Island water supplies, analyses, 260
Catskill water supplies, 258
  analyses, 260
Caustic soda, 89
  analysis, 90
  by causticizing, 89
  distribution, 104
  electrolytic, 89, 91
  in soap making, 91
Caustic soda cells, 91
  Allen-Moore, 99
  Billiter, 103
  Castner, 102
  Diaphragm, 96
  Dow Bi-polar, 91
  Gibbs, 98
  Hargreaves-Bird, 99
  Hooker, 96, 97
  I. C. I.-Wyandotte, 102, 91
  I. G. Farben, 102
  Krebs, 103
  Mathiesen, 103
  Mercury, 102
  Nelson, 98
  Sorensen, 102
  Townsend, 94, 96
  Vorce, 99
Celanese dyes, 623
Cellarius stoneware vessel, 73, 105
Cellophane, 464
  moisture proof, 465
Cellosolve,
  acetate, 750
  stearate, 750
Cellular glass, 221
Cellular rubber, 814
Celluloid, 734, 735, 748
Cellulose,
  from wood, 416, 449
  plastics, 735, 747, 749
  sponge, 465
  xanthate, 448, 450
Celotex, 474, 482
Centrifugal, paper stock cleaning, 436
Centrifugals, 870, 477
Ceramics, 177
  stoneware, 184
  whiteware, 178
Cerium, 989, 976
Cetane rating, 520
Channel black, 671
Charcoal, 225, 317, 319, 320, 717, 726
Chemical factors other than explosives in warfare, 723
  Doron, 733

Chemical factors other than explosives in warfare,
gas mask and adsorbents, 726
goop, 731
incendiaries, 729
Napalm, 731
Pyrogel, 732
Reuben cell, 733
screening smokes, 728
screening smokes table, 730
war gases, 724
war gases table, 725
thermate, 732
Chemico,
ammonia oxidation converter, 127
concentrator, 36, 37
converter, 27
contact mass, 32
nitric acid plant, 127
sulfuric acid plant, 23, 24
Chemigum N, 811
Chile saltpeter, 43, 44
Chinawood oil, 639
Chip machine, 876
Chlordane, 792
Chlorex, 521
Chlorine, 89, 97
allocations, 107
electrolytic, 104, 92
gaseous, and bleach, 107
non-electrolytic, 105, 106
potable water treatment, 254, 257
sewage treatment, 268
shipping, 106
war gas, 723, 725, 726
Chlorobenzene, 590, 754
Chloropicrin, 794, 727, 725
Chloroprene, 811
Chrome Brown, 604
Chrome Fast Black PV, 604
Chrome green, 673
Chrome tanning, 763
Chrome yellow, 673
Chromic acid, 360
Chromium, 971
Chromotrope 2R, 602
Chromotrope 6B, 602
Chromotropic acid, 593
Chrysoidine, 601
Cinnamic aldehyde, 649
Citral, 648, 650, 651
Citric acid, 413
Citronella, oil of, 651
Civet, 652
Claude process, for ammonia, 122
for hydrogen, 371
neon signs, 385
Clay,
ball clay, 178
china clay, 178
catalyst pellets, 508, 554, 556
fluid catalyst, 510
in pyrometric cones, 911
Cloth Red 2R, 603
Cloth Red B, 603
Coal,
anthracite, 225, 226
bituminous, 225, 226
coke, 225
distribution of bituminous, 228
Coal,
composition, 226
deposits, 225
heat value, 226
origin, 225
powdered, 233
prices, 225
production, 225
relative importance, 227
Coal,
shaft-mined, 228
strip-mined, 228, 225
underground, 220
Coal tar, 277, 278, 280, 284
distillation into crudes, 287
refining of crudes, 290
table of crudes, 291
Coal tar, 277, 280, 284
distillation, 287, 290, 291
dyes, 580
products, crudes, 291, 580
Cocaine, 656, 657
Coconut oil, 636, 635
Cod-liver oil, 640, 635, 655
Coke ovens,
beehive, 277
by-product type, 278
Foundation, 284
Glover and West, 278
Koppers, 278
Otto, 278, 284
Piette, 284
Roberts, 284
Semet-Solvay, 278, 279
Wilputte, 284
Woodhall-Duckham, 278
Coke oven gas, 277
ammonia extraction, 281
cooling and purifying, 281
Koppers system, 283
Liquid purification, 284
purifying boxes, 283
Coking retorts,
Glover and West, 278
Woodhall-Duckham, 278
Colchicine, 793
Cold, production of, 242
Collagen, 766
Collins, Dr. S. C., collaborator, 379, 380, 384
Color photography, 778
Colorado river water, analysis, 261
Columbium, 972
Combustible and illuminating gas, 298
coal gas, 278, 281
coke oven gas, 281, 299
composition, table, 299
laboratory gas, 306
natural gas, 227, 298, 299, 303, 514, 524
oil gas, 302
Pintsch gas, 306
producer gas, 302

Combustible and illuminating gas,
sewage digestion gas, 269
water gas, 300
wood gas, 319, 322
Compreg, 743
Compressed gas, 305, 307
Compressors, 850
Congo copal, 676
Contact insecticides, 789
Conveyor, 880
Copper, 957, 958, 973, 896
Corhart blocks, 208
Corn oil, 483, 633, 750
Corn sugar, 484
syrup, 484
Cotton, 566
dye acceptance, 569
Cottonseed oil, 634, 750
Cottrell precipitator, 872, 34, 156
Courmarin, 650
Cream of tartar, 144
Creosote oil, 290, 321, 799
Crocein acid, 589
Crucible steel, 954
Crushers, 879
Crushing rolls, 883
Crutcher, 690
Cryolite, 347
Crystal Violet, 612
Crystallizer, 870, 868
Crystolon, 335
Cuno filter, 862
Cyanamide, 124, 383, 341
Cycling plant, 513
Cyclohexane, 559
Cyclohexanol, 462
Cyclonite, 714
Cylinder stock, 495, 501

D

Danner machine, 218
Darco, 480
D D, 794
D D T, 791, 798
De-Acidite, 265
Dead sea, 156
Decalin, 559
Decolorizing chars, 901
Decomposition voltage, 91, 357, 366
Deep-etch process, 784
Denatured alcohol, 396, 405
Design formation, 576
Detergents, 701
Developed dyes, 571
Dextrin, 482, 484
Diacetyl, 654
Diamond Black F, 605
Diastase, 398, 400, 406
Diatomaceous earth, 901, 319
Dicyclopentadiene, 292
Diels-Alder reaction, 639
Dings, 874
Dioctyl Phthalate, 746
Dioxane, 549
Dipentene, 311
Diphenyl boiler, 231
Diphenyl oxide boiler, 231
Direct Blue 2B, 607
Direct Blue NR, 607
Direct Black, 609
Direct Green, 608
Direct dyeing with acid dyes, 574
Direct dyeing with basic dyes, 575
Direct dyes, 574, 575
Direct Red J, 608
Direct Violet, 609
Disclaimers and Reissues, 839
Disinfectant, 799
Disintegrator, 885
Distillation of coal, 277
beehive ovens, 277
by-product coke ovens, 278
pictorial flowsheet, 280
products, tabulation, 284
Doron, 733
Dorr classifier, 961
Dorr thickeners, 353
Dorrco filter, 861
Dow magnesium plant, 353
Dowfume M, 794
Downs cell, 356, 357
Downs, Charles Raymond, collaborator, 382
Dryers,
cabinet, 866
rotary, 870
shelf, 585
vacuum, 869, 585
Dry Ice, 245
Dry quenching of coke, 281
Duo-Sol process, 522
Duponol WA, 702
Duralumin, 351
Duriron, 896
Durol Black, 604
Dust collector, 871
Dye application, 566
Dye intermediates, manufacture of, 580
Dye transfer process for colored prints, 781
Dyes,
for foods, permitted, 621
for synthetic resin products, 620
for textile products, 597
Dynamites, 707, 712

E

Edeleanu process, 500
Edge runner, 887
Edgewood tower, 105
Eisenlohr process, 694
Electric furnace, for steel, 953, 954
for precious metals, 983
see also electrothermal furnace and and electrolytic furnace
Electrodes,
carbon, 331
graphite, 330, 332
green, 331
raw, 331
Electrolux, 242

Electrolytic furnace, 346
Electromagnetic separator, 873, 874
Electromagnetic separator for liquids, 875
Electrometric methods, 919
Electrothermal furnace, 329
Emersol process, 694
Emulsion paints, 675
Enamels, 678
  alkyd-type, 683
Enzymes, 393, 397
Eosine, 613
Epsom salts, 244
Essential oils, 645, 646
Essotane, 307
Ester gum, 743, 681
Ethanol, *see* Alcohol, ethyl
Ethene, *see* Ethylene
Ether, 656, 657
Ethyl acetate, 319, 320
Ethyl alcohol, *see* Alcohol
Ethylbenzene, 828, 829
Ethylene (Ethene), 542, 403, 504, 389, 549, 828
  chlorhydrine, 544
  chloride, 545
  derivatives, tables, 541, 548
  diamine, 549
  glycol, 544
  oxide, 543
Ethylene bromide, 76
Ethylidene diacetate, 326
Ethyne, *see* Acetylene
Ethynylation, 539
Evaporators, 866, 867, 771
Everdur, 315
Explosives, 705, 707
  high, 711
  permissible, 707
  progressive, 705
  propellants, 717, 721
Explosives, chemical, 705
  Dautriche test, 706
  table, 707
Extractive distillation, 826

F

Fabrikoid, 748
Fans, blowers, 849
Farber, Dr. Eduard, collaborator, 309
Fast Black L, 603
Fast Green, 611
Fast Yellow, 601
Fats and oils, for soap making, table, 688
Fats and oils, production, table, 635
Fatty acids, 692, 311, 694, 696
  distillation, 695
  production, 696
  uses, 696
Fauser processes, 123, 131
Ferro-alloys, 954
Fertilizers, 147
  complete, 148
  mixed, 147, 148
  natural organic, 158
  synthetic urea, 158
Fiberglas, 219
Fibers, strength of, table, 454
Filters, 853, 661, 806
Filters, plate-and-frame, 854
Firebricks, 187
Fire extinguisher,
  firefoam, 245
  liquid carbon dioxide, 245
  soda-acid type, 245
  wall type, 245
Fisetin, 312
Fish oil, 640
Fission, atomic, 975, 987
Flaker, 876
Flavors, 645, 653
Flaxseed, 633
Flick centrifugal catch-all, 871
Flock, 460
Florida water, 653
Flue gas analysis, 232
Fluid catalyst cracking process, 510
Fluorescein, 613
Fluorine, 52, 148
Fluosilicic acid, 52
Food dyes, permitted coal-tar, 621
Foods, quick freezing of, 247
  transportation, 384
Ford continuous sheet process, 213
Ford wood distillation plant, 319
Foreign statutes, 840
Formaldehyde, 755, 798
Formaldehyde dyes, 623, 625
Fourdrinier papermaking machine, 436, 437, 438, 440
Fowler, A. Robert, 705, 723
Fränkl, 374
Frary metal, 973
Freon, 242, 793
Frozen foods, 247
Fuchsine, 611
Fuel oil, 519
Fuels, 224
  relative importance, 227
Fuller-Kinyon pump, 880, 168
Fumigants, 793, 798, 727
Fungicides, 794
Furfuraldehyde, 463, 464, 739
Furnace black, 671
Fusel oil, 397
Fusible alloys, 973

G

G acid, 590
Garden hose and heels, 822
Gardinols, 702
Gas, combustible, *see* Combustible
Gasoline, 496, 500, 513
  cracked, 504
  natural, 512
  polymer, 519
  straight, 495
  100 octane, 515
  synthetic, 524
Gasoline,
  processes for producing, 502
  processes for purifying, 500
Gay-Lussac tower, 3, 5

Gelatine, 759, 765, 768
Girbotol, 287
Glass, 194
  alabaster, 205
  architectural, 213
  cellular, 221
  chemical, 202
  colored, 203
  crown, 197
  fibrous, 219
  flint, 197, 198
  Florentine, 213
  frosted, 194, 219
  obscured, 221
  opal, 205
  optical, 197, 198, 214
  photosensitive, 220
  plate, 212
  potash-lead oxide, 198, 385
  pressed, 217
  safety, 213
  silica, 899, 910
  soda-lime, 197, 199, 201
  structural, 213
  thermal, 213
  tubing, 218
  window, 205
  wire, 214
Glass blocks, 214
Glass, composition, for containers, 199, 201
Glass containers manufacture,
  blow and blow process, 216
  feeder, 216
  press and blow process, 217
  Two Table machine, 216
Glass furnace, continuous, 208, 207
Glass-lined containers, 902
Glass making, history, map, 194, 195
Glass, optical, constants vs. types, diagram, 198
Glass, soda-lime, composition diagram, 199
Glass, soda-lime, melting reactions, 201
Glass, window, manufacture,
  cylinders, 205
  Colburn, 206
  Fourcault, 207
Glauber salt, 73
Glover tower, 3, 4, 8, 10
Glucose, commercial, 483
  crystals, dextrose, 484
  syrup, 484
Glue, 759, 768
Glutamic acid, 482
Glycerin, 686, 698, 741, 743
  process, for alcohol absolute, 409
  recovery and refining, 698, 699
  secondary product, 397
Glycol esters, 545
  ethers, 546
  nitrates, 546
Gold, 975, 976
GR-A, acrylic rubber, 811
GR-I, butyl rubber, 810
GR-M, neoprene, 811
GR-S, all-purpose rubber, 804
Grande Coulée dam, 237
Graphite, artificial, 329, 333, 96, 97
  bulk, 334
  electrodes, 332
Grease, 766, 687, 688
Grillo-Schroeder, 31
Groundwood pulp, 416
Guano, 158
Guggenheim system, 44
Guillaume process, 400
Gutmann system for nitric acid, 45
Gypsum, 173
  gypsum plaster, 173
  gypsum products, 175
Gyratory crusher, 882

H

H acid, 593, 595
Haber process, 120
Haleite, 715
Hall process, 346, 348
Halogenation, 590
Halowax, 748
Hammermill, rotary, 884
Hansa Yellows, 623, 624
Harper fourdrinier, 440
Hastelloy B, 991
Heat exchanger,
  reversing, 380
  unbalanced reversing, 381
Heavy water, 267, 987
Heliarc welding, 373, 384
Helium, 369, 373, 385
Hemlock, Western, 312
Heptane, 514, 515
Herbicide, 793
Héroult, 347
Herreshoff burner, 33
Hevea rubber, 815
Hexachlorobenzene, *see* hexachlorocyclohexane
Hexachlorocyclohexane, 792
Hexachloroethane, 729, 537
Heylandt cycle, 378
Hollander, beater, for papermaking, 432, 433
Hoopes process, 352
Horak, William, collaborator, 177
Hot Actification process, Koppers, 286
Houdriflow process, 508
Houdry catalytic process, 505
Hum-mer, 889
Hycar, 811
Hydrochloric acid, 70
Hydrocyanic acid, 794
Hydroelectric power projects,
  capacities, 236
  location, 236
  relative importance, graph, 227
  table, 236
Hydrofluoric acid, 49
  anhydrous, 51, 517
Hydroforming naphthas, 517
Hydrogen, 369
  by-product, 92, 98, 102, 104, 412
  electrolysis, 371

Hydrogen,
ferrosilicon process, 373
steam on iron, 371
water gas process, 370
water gas and steam process, 370
Hydrogenation, 520, 642
Hydrogen peroxide, 361
concentrated, 363
German process, 364
in rockets, 721
in V-1 bombs, 365, 721
ninety per cent, 364
thirty per cent, 361, 428
Hydrometer, 904
Hydrone, 373
Hydrone Blue R, 619
Hypersorption process, 542

I

I acid, *see* J acid
Iceless refrigerators, 247
Imhoff tank, 269
Indanthrene (blue), 619
Indanthrene Brilliant Green B, 619
Indanthrene Dark Blue BO, 619
Indigo (blue), 617
Indigo White, 617
Indigosols (IG), 618
Indium extraction, 967
Industrial alcohol, 395, 409
by fermentation, 395, 399
from corn, 397
from molasses, 396
production and cost, 404
synthetic, 403
Industrial gases, 369
Industrial waste treatment, 274
Infringement, 840
Insecticides, 786, 798
Instruments of control, 904
Interferences, 837
Intermediates, *see* Dye intermediates
Invertase, 397
Iodine, 47
Ion-exchange adsorbers, 265, 266
anion exchangers, 266
cation exchangers, 266
in sugar refining, 480
synthetic resins, from, 735
Ipatieff, Dr. V. N., 51
Iron oxide, 672
Iso-octane, *see* Octane

J

J acid, 593, 595
Japans, baking, 677
Jasmin concrete, 647
Jaw crusher, 883
Jena glass, 203, 386
Johns conveyor, 880
Jordan, 433, 434

K

Kainite, 151
Kalbperry, 36
Kansas City water supply, 260
Karbate, 334
Karo, 484
Kauri, 676
Kel-F, 750
Kelly filter press, 857
Kerosine, 519
Ketene, 326
Keyes, Donald B., process, 407
Kiln,
cement kiln, 165
lime kiln, 171
pottery kiln, 182
round down-draft kiln, 187
shaft kiln, 171
tunnel kiln, 185, 184
Kleinschmidt compression system, 238
Kodachrome, 779
Kodacolor, 779
Kodak Fluorescence Process, 784
Kraft board, 431
paper, 432
pulp, 432
Krase process, 160
Krebs mercury caustic cell, 103

L

Lacquer enamels, 678, 683
Lacquers, 679
Lactic acid, 413
Laminates, 742, 743
Lamp black, 671, 672, 683
Lamps,
fluorescent, 386
Mazda F, 386
Lanital, 460
Lard and lard oil, 640, 635
Latex foam, 814
Latex, rubber, 823
Latta, James E., collaborator, 525
Lavender oil, 645, 648
Lavender water, 653
Lead, 957, 963, 973, 895
Lead arsenate, 788
Leather, 759
Lepol kiln, 168
Leucite, 156
Lignin, 309, 313, 316
Lignite, 224, 226, 228, 225
Lime, 170
hydrated, 173
Linde, 377, 379
Linde-Fränkl, 379, 381
Linseed oil, 630, 674, 676, 683
Liquid purification of coal gas, 284
Girbotol, 287
Hot Actification, 286
Koppers, phenolate, 286
Thylox, 287
Shell phosphate, 287
sodium carbonate, 284
Litharge, 671
Lithography, 782
Lithopone, 669
Logwood, 312, 764, 570

Low-temperature carbonization, 293
L. P. G. liquefied petroleum hydrocarbons, 512, 513, 305
Lubricating oils, 501, 502, 520, 521, 523
Lucidol, 358
Lucite, 734, 746
Lunge, Georg, 12
Lunge tower, 45
Lustron, 735

M

Magnesium, 352
  carbothermic process, 354
  electrolytic process, 352, 353, 354
Magnesium alloys, 354
Magnesium fluosilicate, 169
Magnesium oxychloride cements, 175
Magnetic pulley, 874
Malachite Green, 612
Maleated oil, 639
Maleic acid, 561
Maleic alkyds, 741, 742
Malic acid, 562
Malt, 400
Maltase, 398
Maltol, 317
Maltose, 398, 484
Manilla copal, 676
Mannheim salt-cake furnace, 67
Mannheim system for sulf. trioxide, 31
Massecuite, 477, 479
Mass filter, 863, 767
Materials of construction, 891
Mechanical stokers, 232
Melamine, 741
Melamine-formaldehyde resins, 741
Mepacrine, 656
Mercury, 957, 969, 973
Mercury vapor boiler, 240
Merpol, 702
Methane, 299, 504, 543, 526
Metanil Yellow, 601
Methadon, 658
Methanol, from wood, 317, 319, 324, 325
  synthetic, 551
Methyl acetate, 319
Methyl alcohol, *see* Methanol
Methyl ethyl ketone, 319, 519
Methylene Blue, 615
Methyl Orange, 602
Miami Tugboat Pulper, 434
Milorganite, 158, 273
Milwaukee sewage disposal plant, 272
Mine-mouth steam plants, 240
Mitchell, J. E., reviewer, 828
Mixed acid, 48
Molasses, 396, 404
Molding compound, 739
Molybdenum, 972
Monastral Fast Blue BS, 623
Monel metal, 897
Monosodium-l-glutamate, 482
Mordanting, with tannin, 574
Mordants, metallic, 575
Morrell, Dr. C. E., collaborator, 825
Motor fuel, table, 513
  sources, 502
  sources, other than petroleum, 524, 405 528
Mucilage, 770
Musk, 652
  artificial, 652
Mustard gas, 727, 725

N

Nacconol NR, 702
Napalm, 731
Naphtha, 496, 499, 500, 501, 504
Naphthalene, 290, 291, 580, 583, 585, 595, 560, 693
Naphthenes, 495
Naphthionic acid, 589
Naphthol, α and β, 592, 599
Naphthol AS, 571, 572
Naphthols, 624
Nash Hytor, 105, 851
Natural gas, 303, 227, 286, 298, 514, 524, 671, 672
  storage, 305
Natural gasoline, 512
Naval stores, 310
Nematocides, 794
Neo-Fat D-142, 694
Neohexane, 516
Neolan dyes, 623
Neoprene, 811
Neptunium, 986
Neradols, 763
Neroli, oil of, 648
Neutron, 975, 986
New Orleans water supply, 260
Newsprint, 416, 432, 440
New York City water supplies, 258
Niagara Falls power,
  application of water, 234
  generator assembly, 235
  water wheel, 235
Nichols, Dr. William H., frontispiece
Nickel, 969
Nicotine, 790
Nitraprills, 150
Nitration, 581, 711, 713, 715, 718
Nitrator, 583
Nitre cake, 45, 66
  uses, 67
Nitric acid, 43
  bleached, 46
  concentration, 129, 130
  properties, 47
  systems,
    Gutmann, Hough, Skogland, 45
Nitric acid from ammonia oxidation, 126
  from Chilean nitrate, 43
  from synthetic nitrate, 45
Nitrobenzene, 584, 585, 586
Nitrocellulose, manufacture, 717
  ball-powder process, 718
  perforated-grain powders, 718
  properties, 709
Nitrogen, 374, 383

Nitrogen fertilizers, consumption, 150
Nitrogen fixation, 111
  ammonia processes, 114
  cyanamide process, 124
  electric arc processes, 114
  nitride process, 126
Nitrogen products, natural, 147
  synthetic, 111
Nitroglycerine, 711
Nitrosyl process, 105
Nitrous oxide, 387
Norit, 480
Novadelox, 358
Novocaine, 656
Novolac, 739
Nylon, 460

O

Octane,
  iso-octane, 495, 514, 515, 516
Octane number, 514
Octylene,
  iso-octylene, 516
Oil Red EG, 609
Oiticica oil, 676
Oleic acid, 629, 696, 693
Oleomargarine, 641
Oleum, 25, 30, 21
Olive oil, 633
Oliver filter, 859, 806
Open hearth steel, 937
Optical pyrometer, 910
Orange I, 601
Orange IV, 601
Osalid, 785
Ossein, 766
Owens bottle blowing machine, 215
Oxalic acid, 54
Oxo process, 545
Oxyacetylene torch, 389
Oxygen, 373
  gas, 374
  liquid, 378
  processes, 374
  tonnage, 374, 379, 382
Ozokerite, 528

P

Pachuca, 971
Paints, 666, 673
Palatine Chrome Black, 604
Palm oil, 634
Paludrin, 656
Paper, 416, 440
Paper mills, 416
Papermaking machine,
  cylinder, 439, 440
  fourdrinier, 436
  Harper, 440
  Yankee, 440
Paradichlorobenzene, 590
Paraldehyde, 656
Paris green, 789
Patchouli, 648
Patent publications and services, 842
Patents, 833
Peanut oil, 633
Pebble mill, 886
Penicillin, 658
Pentalyn, 675
Peppermint, oil of, 646
  American, Menthae piperita, 646
  Japanese, Menthae arvensis, 646
Perbunan, 811
Perchloron, 109
Persulfuric acid, 361
Petrochemicals, 529
Petroleum, 487
  crude, 487
  prospecting for, 487
  refining, 496
  reserves, 490
  transportation, 492
Petroleum, crude,
  classification, 494, 495
  distillation, 496, 499, 501
  production, 493
  transportation, 492
Petroleum products, refined, table, 523
Pharmaceuticals, 655
Phenanthrene, 290
Phenol,
  natural, 291
  synthetic, 592, 753
Phenolformaldehyde condensation product, 737
Philgas, 307
Phosgene, 726
Phosphate rock, 134
  deposits, 134
  ground fine, 135
  production, 135
Phosphine, 614
Phosphoric acid, 139
  thermal methods, 139
  wet method, 139
Phosphorus, 140, 141
Phosphorus pentoxide, 140, 141
Phosphate,
  ammonium, 143
  diammonium, 143
  disodium, 142
  lithium, 142, 155
  monocalcium, 143, 136
  monosodium, 142
  slag, 148
  tricalcium, 134, 148
  trisodium, 141, 232
Photographic film base, 748, 776
Photographic films, 773
Photographic paper, 776
Photographic plates, 776
Phthalate esters, plasticizers, 749, 746
Phthalic anhydride, 560, 594, 742
Phthalocyanines, 622, 673
Picramic acid, 604
Picric acid, 715, 708
Pig iron, 924
Pigments, 666
  colored, 671

Pilatus dyes, 623
Pimaric acid, 310
Pimelic acid, 464
Pinene, 310
Pine oil, 311
Pine tar, 311
Pinoline, 683
Pipe lines,
  for natural gas, 304
  for petroleum crude, 492
  for refinery products, 492, 305
Piperonal, 650
Pitch, 287, 288, 291
Pitot tube, 916
Plasmoquin, 656
Plastic bottles, 752
Plasticizers, 681, 749, 746
Plastics, 734, 742
Platinum, 975, 982
Plexiglas, 734, 746
Plutonium, 975, 986, 987, 988
Poidometer, 881
Polar or Milling dyes, 623
Polyethylene, 746
Polyflex, 752
Polyhalite, 151
Polymerization products, resins, 764
  methyl methacrylate resins, 746
  polyethylene, 746, 752
  polystyrene, 747
  vinyl resins, 746
Polymer structure, 809
Pomade, Jasmin absolute, 648, 649
Ponceau R, 602
Portland cement, 163
  high early strength, 170
Potassium alum, 54
Potassium dichromate, 360
Potassium formate, 54
Potassium permanganate, 359, 721
Potassium persulfate, 362
Potassium salts, 150
  deposits, 151, 152
  from brines, 153
  from cement kilns, 156
Powdered coal, bituminous, 233
Power, electrical,
  capacities of major products, 236
  hydroelectric, 233, 227
  relative prices, 241
  steam-generated, 236
Printing inks, 683
Procaine, 656, 658
Propane, 306, 510, 512, 542
  liquid, 521, 305
Propargyl alcohol, 539
Propellants, 717, 721
  for rockets, 719
Propylene, 325, 504, 519, 700
Protective coatings, 673, 678, 735
Protozoa, 393
Prussian blue, 672, 683
Pulp fiber, screening, 426
Pulp mills, 416
Pumps, 844
Purifying boxes, 283
Pyramine Orange R, 608
Pyrazolone dyes, 610
Pyrethrine, 793
Pyrethrum, 791
Pyrex glass, 203, 386, 899, 910
Pyridine, 290, 291, 292
Pyrobor, 155
Pyrofax, 307
Pyrogel (goop), 731
Pyroligneous acid, 317, 319, 323
Pyrolusite, 360
Pyrometric cones, 190
Pyrophoric alloys, 976
Pyroxylin, 717, 682, 748

Q

Quebec, Eastern, titanium deposits, 669
Quinacrine, 656
Quinine, 656

R

R acid, 590
Radiation pyrometer, 909
Radium, 975, 984, 986
Raney nickel, 643
Rapidogen, 623
Rare gases, 385
Raschig method, for phenol, 754
Rasorite, 156
Raymond mill, 886
Rayon, 443
  acetate, 455
  cuprammonium, 457
  dye acceptance, 567
  filament, 444, 453
  flock, 460
  staple fiber, 458
  tow, 460
  viscose, 446
  viscose flowsheet, 447
Rayon, spinning processes
  bobbin, 453
  continuous, 454, 455
  Godet wheel, 453
  pot, 453
R D X, 714
Reclaimed rubber, 814
Red lead, 671
Redler conveyor, 880
Redox system, 809
Reduction, 584
Refractories, 188
Refrigeration, 244
Refrigeration, agents, table, 242
Refrigerators
  iceless, 247
  silica gel, 248
Reppe chemistry, 538, 544
Reppe, Dr. Julius Walter, 538
Resin acids, 311
Resins, fossil, 676
Resins, synthetic, 734
  casting resins, 740
  hollow ware, blown, 752

Resins, synthetic,
molding compound, 739, 745
protective coatings, 735, 742, 682, 678
stretch-orientation, 751
Resin varnish, 742, 676
Resistance pyrometer, 909
Resorcinol, 592, 740
Rezyl, 743
Rhodamine B, 613
Ringle, William G., collaborator, 666
Ripple enamel, 678
Rocket propulsion, 719
Rodenticides, 794
Rope, 459
Rosaniline, 612
Rose absolute, 647
Rose concrete, 647
Rosin, 309, 310, 676, 688, 690
Rosin esters, 743, 744
Rosin oil, 683
Rosin varnish, 742, 676, 683
Rotameter, 918
Rotary suction filter, 859, 696
disk type, 861
drum type, 859
Rotex, 888
Rouget, 379
Rubber, 802
natural, 803
synthetic, 803, 804
Rubber belting, 821
Rubber compounding, 817
Rubber-lined tanks, 896
Rubber stock preparation, 818
Ruby, 338
synthetic, 389

S

Saccharin, 656
Safranine, 614
Saggers, 181
Salicylic acid, 594
Sal soda, 64
Salt, 56, 58, 59, 66, 67, 606, 686
brines, 57
deposits, 56, 58
evaporation, 57
recovered, 101
rock salt, 56
solar, 57
statistics, 58
uses, 58
varieties, 56, 57, 58
Salt cake, 66
mechanical furnace for, 67
synthetic, 70
Salvarsan, 656
Sandalwood, 312
Sand filter, 256
Santomerse 1, 702
Sapphire, 338
Schaeffer's acid, 589
Schickert plant, 364
Screening smokes, 728
Screens,
electrically vibrated, 889
flat, with tapping, 888
hand, 888
Seagram, Joseph E., and Sons, flowsheet, 399
Searches, 838
Searles Lake, 153
Self-sealing fuel tank, 822
Semesan, 794
Separator, Rowand-Wetherill, 874
Servel, 242
Sewage disposal, 267
disinfection, 268
primary treatment, 267
secondary treatment, 268
activated sludge process, 268
trickling filter, 268
solids disposal, 268
Sewage disposal plants
Buffalo, 270, 271
Milwaukee, 272
Worcester, 269
Shanks system, 44
Sharp, Donald E., collaborator, 194
Shell-and-leaves type filter press, 856
Shop rights, 841
Signs
fluorescent, 386
luminous, 386
neon, 385
Silica, fused, ware, 898
Silica gel, 248
Silicate of soda, *see* Sodium silicate
Silicon carbide, 334, 337
Silicone resins, 750
Sillimanite refractories, 188
Silver, 975, 980
Skimming unit, continuous distillation, 499
Sky Blue FF, 607
Smoke pot, 729
Soap, 686
boiled process, 687
cold process, soap, 691
kettle soap, 690
laundry soap, 689
materials for manufacture of, table, 688
milled toilet soap, 690
miscellaneous soaps, 692
textile soap, 692
Soap powder, 692
Soda ash, 58, 59, 62, 64, 155, 690, 692
Leblanc process, 70
natural, 65
Solvay process, 59
Sodamide, 359, 617
Soda recovery, paper mill, 421, 422
Soday, Frank. J., contributor, 804
Söderberg electrode, 333
Sodic aluminum sulfate, 53, 143
Sodium, 355
Sodium bicarbonate, 62, 64, 144
Sodium bisulfite, 84
anhydrous, 86
Sodium carbonate, 57, 59, 64, *see* Soda ash

Sodium chlorate, 360
Sodium chloride, *see* Salt.
Sodium chlorite, 109, 358, 255
Sodium cyanide, 359
Sodium hydride, 359
Sodium hydroxide, *see* Caustic soda.
Sodium hyposulfite (hydrosulfite), 87
Sodium lamp, 386
Sodium nitrate, 43
  solid pellets, 150
  synthetic, 131
Sodium nitrite, 131
Sodium oxalate, 54
Sodium peroxide, 358, 363, 428
Sodium silicate, 74, 770, 690
Sodium sulfate, 66
  natural, 65, 70, 155
Sodium sulfide, 80
  by-product, 85
Sodium sulfite, 84
Sodium thiosulfate (hypo), 83
Soledons (ICI), 618
Solvay soda, 59
Solvent purification of lube fractions, 521
Solvents for lacquer, 682
Solvents for paints, 674
Soybean oil, 636, 676
Sperm oil, 642
Spirit Yellow, 601
Sponge, cellulose, 465
Sponge iron, 934
Sponge rubber, 824
Sprowls, J. B., reviewer, 645
Stable Diazo Salts, 623
Stafford retorts, 318, 322
Starch, from corn, 483
Steam boilers, 229
  fire tube, 230
  furnace, water-cooled, 237
  high pressure, 239
  mechanical compression of steam, 238
  mercury vapor, 240
  water tube, 229
Stearic acid, 686, 696
Stearns magnetic separator, 873
Steel, 936, 893
Steuben ware, 214
Stilbene dyes, 610
Stomach poisons, 787
Stoneware, 896, 73, 105
  for HCl absorption, 71
  nitric acid condensing, 47
  Cellarius vessel, 73
Stratco alkylation contactor, 518
Streptomycin, 664
Styrenated oil, 639
Styrene, 828
Styron, 735
Succinic acid, 562
Sucher, 480
Sucroblanc, 480
Suction filter, 858, 859, 861
Sugar, 468
  beet sugar, 468, 481
  cane sugar, 468, 472
Sugar,
  corn sugar, 484
  direct consumption sugar, 479
  invert sugar, 472
  raw, 479
  refining, 479, 480
Sugars, from wood, 313, 316, 317
Suida process, 323
Sulfan, 27, 21
Sulfanilamide, 658
Sulfanilic acid, 588, 589
Sulfathiazole, 658
Sulfonated oils, 703
Sulfonation, 587
Sulfonator, 587
Sulfur, 795
  brimstone, 1, 8, 14
  burners, 8, 23, 3, 7
  by-product, 287
  elemental sulfur, mfr'd, 32, 796
  for sulfide liquor, 85
  for sulfite liquor, 83, 420
  fungicide, 795
  in lime-sulfur, 790
  production, 796
  sulfuric acid mfre, 3, 23, 7, 8
  uses, 796
  vulcanizing agent, 816
Sulfur dioxide, 13, 4, 7, 83
  liquefied, 387
  refrigerant, 242
  uses, of liquefied, 500, 521
Sulfur dyes, 620
Sulfur trioxide, 21, 26, 27
  for smoke screens
Sulfuric acid, 1, 20
  distribution, 38
  heat rise test, 30
  properties, 35, 34
Sulfuric acid manufacture,
  chamber process, 1
  concentration, 35
  contact process, 20
  cyclic process, Trail, 31
  Gaillard-Parrish chamber, 15
  Mills-Packard chambers, 15
  nitric oxide pressure process, 13
  nitric oxide process, 12
  space efficiency for chambers, 17
  towerless plant, 15
  towers process, 15
Sumach, 312
Sun Yellow, 610
Superphosphate
  ammoniated, 149
  ordinary, 136
  triple, 138
Surface-active agents, 701
Surface combustion, 307
Sweetland filter press, 858
Swerl, 702
Sylphrap, 464
Sylvinite, 152
Symons, Dr. George E., collaborator, 251
Syntans, 763

Synthetic beads, catalyst, 509
Synthesis gas, 525
Synthetic enamels, alkyd-type, 683
Synthetic ethyl alcohol, 403
Synthetic glycerin, 700
Synthetic liquid fuels, 524
Synthetic medicinals, production, table, 658
Synthetic methyl alcohol, 551
Synthetic organic chemicals, 533
Synthetic organic insecticides, 791
Synthetic plastics, 734
Synthetic resins, 734
  by condensation, 737
  by degradation, 747
  by polymerization, 746
  dyes for, 620
  uses, table, 735
Synthetic rubbers, mfg., 804
Synthetic textile fibers, 443
Synthine process, 527

T

Tall oil, 311, 694, 688, 744
Tanning agents, 761, 762, 763
Tannins and dyestuffs, from wood, 312
Tantalum, 972
Tar
  coal tar, 277, 280, 284
  distillation, 287, 290, 291
  petroleum tar, 523
  wood tar, 320, 321
Tarkington, Raife G., reviewer, 773
Tartaric acid, 143, 144
Tartrazine, 610, 611
Technicolor, 782
Teflon, 750
Teglac, 743
Temperature measurements, 906
Tenite I, 751
Tentelew, 31
Terpineol, 405, 655
Tetraethyl lead, 76
Tetrahydrofuran, 463, 539
Tetralin, 559
Tetryl, 715
Theis, Edwin R., 759
Thermal conductivity cell for gases, 912
Thermal cracking, 503, 651
Thermocouples, 907
Thermofor Catalytic Cracking, TCC, 506
Thermofor Pyrolytic Cracking, TPC, 504
Thermopane, 213
Thioindigo, 617
Thiokol, 813
Thomas calorimeter, 284
Thomas meter, 283
Thorium, 989, 976, 988
Thylox process, 287
Tin, 957, 968, 973
Titanium dioxide, 669, 450, 456, 461, 691
Titanium tetrachloride, 729
T N T, 713, 707
Toilet water, 653
Toluene, 290, 291, 582, 583
  from petroleum, 519
  production, 595
Toluylene Orange R, 608
Tonnage oxygen, 374. 379, 382, 525
Toussaint, W. J., collaborator, 824
Tow, rayon, 460
Tower packing, 900
Transferrer, of heat, 31
Transparit, 464
Tributyl phosphate, 681
Trichloroethylene, 536
Tricresyl phosphate, 681
Trioxane, 549
Triphenylmethane dyes, 611
Triton X-400, 702
Tung oil, 639, 675, 676
Tungsten, 988
Tungstic acid, 988
Turkey Red oil, 638
Turpentine, 309, 674, 757
Twitchell process, 692
2-4-D, 793

U

Ultipara, 809
Underground storage, for natural gas, 306
Unionmelt, 390
Unit operations and unit processes, 920
Uranium. 975, 984, 985, 986
Urea, 740
  synthetic, 158
Ureaformaldehyde condensation product, 740

V

Vallez filter, 862
Valve, barrel, 319
Valves and pulleys, 851
Vanadium, 990
Vanadium pentoxide, catalyst mass, 20, 23, 756
Vanillin, 649, 650, 654
Van Ruymbeke, Joseph, process, 409
Varnish resins, 676
Varnishes, 675
  resin varnish, 742
Vat dyes, 616
Vegetable oils, 633
  production, 635
Venturi tube, 917
Veronal, 656
Vetivert, oil, 648
Victoria Blue, 612
Vinegar, 414
Vinyl acetylene, 537
Vinylation, 539
Vinyl chloride, 534
Vinyledene, 746
Vinylite, 746
Viscose, 450
  process, 446
  rayon, 443
  solution, 450, 452
  sponge, 465
Viscosity index, 521
Vistanex, 810

Vitrified enamel, 190
Volumetric meters, 284
Vorticella, 273, 274
Votator, 698
Vulcalock, 896
Vulcanization, 816
Vycor, 203

W

War gases, 723, 724
Water, for chemical plants, 261, 455
  for Thermofor bead plant, 265
Water for municipal and industrial use, 251
  chlorination, 254
  classification, 252
  deionization, 264
  disinfection, 254
  distribution, 254
  filtration, 256
  procurement, 252
  purification, 253
  softening, 262
Water, municipal, purification, by
  aeration, 256, 259
  algicides, 256, 259
  alum addition, flocculation, 255, 257
  chlorination, 254
  chlorine dioxide, 254, 255
  coagulation, 253
  filtration, 256
  ozone, 254, 255
  sedimentation, 253
  ultraviolet light, 254, 255
Watersheds for New York City water, map, 258
Water softening, 231
Wax distillate, 501
Waxes, 642, 528, 648, 764
Weizmann process, 411
Wesp, Edward F., collaborator, 443
Weston, Harry E. Weston, collaborator, 416
Wet plate process, 778
Wetting-out agents, 577, 701
Whale oil, 639
White lead, 666
Willamette Valley plant, 313, 314, 317
Wilson, Ralph H., 759
Wood, chemical utilization of, 309
  distillation, 317
  extraction, 309
  hydrolysis, 312
Wood distillation
  batch retorts, 319
  continuous process retorts, 319
  continuous process retorts (new), 322
Wood hydrolysis, materials relation, 315
Wood hydrolysis, processes
  Bergius-Rheinau, 314
  Madison, 315
  Scholler, 315
Wood preparation, for pulp, 418
Wood preservation, 799
Wood pulp, 417, 418
  bleaching, 428
  chemical, 424
  mechanical, 422
  soda pulp, 421, 424, 425
  sulfate, 424, 425
  sulfite, 424, 425
Wool
  artificial, 460
  natural, 567
Wool Fast Blue BL, 614
Worcester sewage. disposal plant, 269
Wort, 407
Wrought iron, 934

XYZ

Xanthate, 448, 449, 450
Xanthene dyes, 613
Xylene, 290, 291
Yeasts and bacteria, activity of, 393
Zac, 208
Zeo-Karb, 264
  —H, 265
Zeolite, 262, 263, 264
  water softener, 263
Zinc, 957, 965, 973
Zinc oxide, 668, 673, 691
Zymase, 397

ALLAMA IQBAL LIBRARY
49895

J. & K. UNIVERSITY LIB.
Acc. No 49895
Date 17.7.64